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SYNTHETIC ASBESTOS INVESTIGATIONS, I: STUDY OF SYNTHETIC FLUOR-TREMOLITE*

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ABSTRACT

A study of synthetic fluor-tremolite by *x*-ray and optical methods was considered basic to research on fluor-amphiboles as potential substitutes for asbestiform minerals.

A review and critique of previous syntheses is given, together with earlier optical and *x*-ray data on both natural hydroxy- and synthetic fluor-tremolite. Optical determinations on chemically analyzed synthetic fluor-tremolite gave the following values:

$\alpha = 1.581 \pm 0.001$ $2V = 86\frac{1}{2}°$
$\beta = 1.593 \pm 0.002$ $Z \wedge c = 21°$
$\gamma = 1.602 \pm 0.002$ Biaxial negative

The values were compared with those for natural hydroxy-tremolite. On an *x*-ray powder pattern of synthetic fluor-tremolite, all resolved maxima were indexed up to 76° 2θ. The following monoclinic cell dimensions were obtained:

$a_0 = 9.781 \pm 0.005$ Å
$b_0 = 18.007 \pm 0.004$
$c_0 = 5.267 \pm 0.006$
$\beta = 75° 29' \pm 5'$

A comparison was made with the values for natural hydroxy-tremolite. Goniometric measurements on well-formed single crystals of synthetic fluor-tremolite gave values in agreement with the calculated figures. Single-crystal *x*-ray patterns (rotation and Weissenberg) were made.

INTRODUCTION

In the course of research on the synthesis of asbestiform minerals, experimentation is being conducted on the crystallization of fluorine-containing amphiboles from melts. The compound fluor-tremolite ($Ca_2Mg_5(Si_4O_{11})_2F_2$) was chosen as a logical starting point because its structure is basic to all of the monoclinic amphiboles. Thus, determination of some of its fundamental constants is necessary as a standard of comparison for other fluor-amphiboles synthesized during the course of this investigation.

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In the present study, particular attention has been given to the synthesis of fluor-tremolite of a known composition, so that a meaningful determination of its x-ray and optical properties could be made.

REVIEW OF PREVIOUS RESEARCH

Ehrenberg (1) attempted to synthesize fluor-tremolite by reacting an appropriate mixture of CaF_2, $CaCO_3$, MgO, and SiO_2 in the solid state. The products formed were identified by x-rays. At 620° C. forsterite formed, and at 750° diopside was observed in addition to forsterite and fluorite. The same phases were observed at 800°, with fluor-tremolite absent in every instance. Ehrenberg came close to synthesizing fluor-tremolite, since with the same raw materials fluor-tremolite was recently prepared at this laboratory by solid-state reaction at temperatures just below the formation of a liquid phase. By crystallization from the melt, fluor-tremolite is readily obtained with these batch components, although diopside and forsterite are invariably present.

In 1935 Grigoriev (2) attempted the synthesis of a fluorine-containing hornblende, utilizing the technique previously found suitable for the synthesis of fluor-micas. The batch used approximated the empirical formula $K_2CaMg_6(AlSi_6)O_{19\frac{1}{2}}F_2$. Equilibrium conditions were not attained because of the continual loss of volatile material from the batch and also because a method of maintaining a constant temperature was lacking. The resulting product contained fluor-phlogopite, spinel, and fluorides, as well as fluor-amphibole. From the composition of the batches, the presence of these other phases is not unexpected. Intergrowth with phlogopite precluded chemical analyses.

A petrographic examination showed the synthetic hornblende crystals to be sharply bounded, with the faces (001), (010), and (110) usually well formed. The angles between the faces were as follows:

$$(010):(1\bar{1}0) = 118^\circ$$
$$(\bar{1}10):(110) = 124^\circ.$$

The optical constants of the synthetic hornblende were reported as

$\alpha = 1.615$ $\gamma - \alpha = 0.021$
$\beta = 1.623$ $2V = 70 - 90^\circ$
$\gamma = 1.636$ Optic plane = (010)

After showing that amphiboles may be synthesized from fluorine-containing silicate melts, Grigoriev, working with Isküll (3), investigated the feasibility of synthesizing amphiboles by melting natural amphiboles to which a fluoride had been added. A hornblende represented by the formula $(Na, K, Ca)_{2.9}(Mg, Fe^{++}, Fe^{+++}, Al, Ti)_5(Al, Si)_8O_{22}(OH, F)_{1.98}$ was fused both with and without an addition of CaF_2. All fusions were made in graphite crucibles at approximately 1350° C. As expected, the fluoride-free melt failed to yield an amphibole; it consisted almost entirely of pyroxene crystals. The melts to which 5% CaF_2 was added resulted in crystallization of an amphibole. Most of the iron originally present was reduced to the metallic state. Unfortunately, no chemical analysis of the reaction product was made.

The optical properties of the regenerated, colorless amphibole were reported as follows:

$\alpha = 1.586 \pm 0.003$	$\gamma - \alpha = 0.017$
$\beta = 1.590 \pm 0.003$	$2V = 55 - 60°$
$\gamma = 1.603 \pm 0.003$	$Z \wedge c = 17°$

The regenerated amphibole gave an x-ray powder pattern similar to the natural material used; no indexing was made.

The dependence of the optical properties of amphiboles on their chemical composition was investigated by Grigoriev (4), using synthetic fluor-amphiboles whose compositions were readily controllable. Four batches composed of CaF_2, MgO, and SiO_2 were compounded in the proportions required for tremolite. To these were added 1, 3, 5, and 10% alumina and the batches melted in carbon crucibles at approximately 1400° C. A microscopic examination indicated amphibole to be the only crystalline phase present. No mention was made of any glassy phase. Recent research in the authors' laboratory with similar batches has always resulted in the crystallization of some diopside and free silica, a small amount of glass, and occasionally, with higher alumina contents, anorthite. As the materials were not especially volatile, Grigoriev did not make a chemical analysis of the final products. This is unfortunate, as the optical data presented would be more significant if the exact compositions of the fluor-amphiboles were known. However, Grigoriev's results show that an increase in Al_2O_3 causes a decrease in α, γ, $\gamma-\alpha$, and the extinction angle.

In the early thirties Lüdke (5) began research on the synthesis of asbestos. Lüdke's process was a type of pneumatolytic technique in which mixtures of alkalies, alkaline earth compounds, silica, and fluorides were heated in an air stream at temperatures below the decomposition temperature of the synthetic amphibole. Undoubtedly, Lüdke's experimentation and small-scale production represent the most extensive effort to date on the synthesis of amphiboles. The severe shortage of asbestos in Germany during World War II gave impetus to his work, and many attempts were made to utilize the amphibole as a substitute for asbestos. In every test, however, the synthetic amphibole was inferior to the natural material. In spite of technical improvements in his process, the quality of the synthetic amphibole asbestos was not improved. The fibers were comparatively brittle and insufficiently resistant to chemical attack, the later primarily due to the high alkali content.

The synthetic amphiboles prepared by the Lüdke process contained both hydroxyl and fluorine and consequently differed from those synthesized by Grigoriev and later investigators. Analyses show that Lüdke's products were comparatively high in sodium, probably similar to richterite and eckermannite in composition.

The index of refraction of one of his synthetic amphiboles was "very close to 1.60," and the extinction angle was 18–19°. *X*-ray powder patterns were similar to those for natural hornblendes, but a detailed indexing was not made.

Bowen and Schairer (6) have synthesized fluor-amphiboles by heating pyroxenes with an addition of a small amount of NaF in evacuated silica tubes. The quantity of amphibole produced was too small to permit a chemical analysis. Inasmuch as the original material was a pure clinoenstatite in one case and a glass of the composition $FeSiO_3$ in the other, the composition of the amphibole synthesized from each of these two end members must have been close to $Mg_7(Si_4O_{11})_2F_2$, and $Fe_7(Si_4O_{11})_2F_2$, respectively. As NaF was added, however, it is reasonable to assume the presence of some sodium in their products. Such a possibility was acknowledged by the investigators in their report, and recent work at this laboratory makes the assumption probable.

Recent work by Van Valkenburg and Pike (7) has indicated that fluortremolite melts incongruently, with forsterite the primary phase. The liquidus temperature was determined as 1350° C., with tremolite forming near 1145°. The exact determination was difficult owing to a tendency for defluorination of the melt.

EXPERIMENTAL PROCEDURES

In the first experiments, specially machined crucibles of approximately 30 cc. capacity with screw-on graphite covers were employed. The charge was melted by heating to 1400° C., maintained at the maximum temperature at least 30 minutes, and then cooled to 1200° C. within 2 hours. The resulting product consisted of acicular crystals of fluor-tremolite, some as long as several millimeters, associated with small amounts of diopside, tridymite, CaF_2, and MgF_2. By this simple method the actual synthesis of fluor-tremolite is readily accomplished. However, for the purpose of this research, single crystals suitable for *x*-ray study and goniometric measurements were required. No such crystals were obtained in the experiments with 20 to 30-gram batches.

It was soon apparent that the manner in which the desired components were added had a definite effect on the fusion temperature and also, particularly when the reaction was confined to the solid state, on the resulting crystalline phases, although in all instances the major crystalline product was fluor-tremolite. In the initial experiments, natural wollastonite, MgF_2, MgO, and finely ground quartz were proportioned to yield fluor-tremolite ($Ca_2Mg_5(Si_4O_{11})_2F_2$). These raw materials melted below 1400° C. The same ultimate composition when prepared from CaF_2, $CaCO_3$, MgO, and finely ground quartz required a temperature in excess of 1450° for melting.

In an attempt to grow larger crystals, batches as large as 20 pounds were crystallized in carbon crucibles, which were in turn sealed into large SiC crucibles and soaked at 1450° C. for 4 to 8 hours in an electric furnace. The rate of cooling of the furnace was varied from 4° to 100° per hour to 1100° C., at which temperature the power was turned off. In every experiment but one the general character of the resulting fluor-tremolite crystals was similar and unfavorable, regardless of the size of the batch or the rate of cooling (providing the cooling was slow enough to permit crystallization).

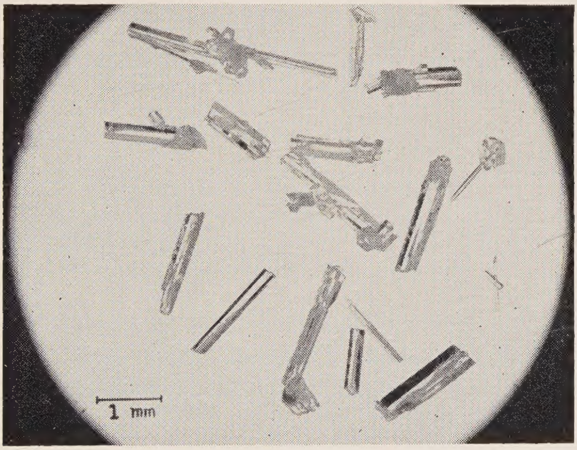

FIG. 1. Photograph of synthetic fluor-tremolite crystals (9×).

In the one crystallization which yielded an abundance of single crystals of remarkable clarity and distinct crystal form, the maximum temperature (1450° C.) was maintained for 4 hours and then lowered at a rate of 5° C. per hour to 1100°. The single crystals (up to 4 mm.) of fluor-tremolite were found in the lower portion of the reaction product, having crystallized from a liquid phase.

Some of these crystals were separated from the mass by hand sorting for *x*-ray and optical studies. A few selected crystals, shown in Fig. 1, were used for goniometric measurements. A portion of the crystallized product was beneficiated by heavy liquid media to obtain a sample of fluor-tremolite pure enough to justify a chemical analysis. Tetrabromoethane and methylene iodide (adjusted to 2.95 and 3.10 gm/cc., respectively) were used to remove a small amount of glass, tridymite, diopside, and CaF_2. The separation effectively removed these impurities, although some MgF_2 attached to fluor-tremolite crystals persisted. The amount of MgF_2 remaining was determined by petrographic analysis to be less than 3%.

RESULTS

(1) *Chemical Composition*

The beneficiated synthetic fluor-tremolite sample was examined optically and found to consist of more than 95% fluor-tremolite, with a small amount (2–3%) of MgF_2. This sample was chemically analyzed, and the results are given in Table 1.

TABLE 1. CHEMICAL ANALYSIS OF SYNTHETIC FLUOR-TREMOLITE (PER CENT)*

Constituent	Theoretical Composition	Actual Composition	Corrected Composition†
SiO_2	58.88	56.86	58.56
MgO	24.69	26.61	25.45
Fe_2O_3	0.00	0.06	0.06
CaO	13.74	12.76	13.14
Na_2O	0.00	0.10	0.10
F^-	4.65	6.30	4.65
$O=F$	−1.96	−2.65	−1.96
	100.00	100.04	100.00

* Analysts: H. R. Shell, R. L. Craig; Sample 3838, dried at 110° C.

† On assumption that fluor-tremolite and MgF_2 are sole phases present; using 22 oxygen and 2 fluorine anions as basis, composition of synthetic fluor-tremolite calculated from analysis as $Na_{0.03}Ca_{1.91}Mg_{5.15}(Si_{3.98}O_{11})_2F_2$, indicating 2.9% MgF_2. Slight excess of Mg^{++} attributed to small amount (<1.0%) of an isotropic phase, probably glass.

From the corrected analysis, the chemical composition of the synthetic fluor-tremolite is seen to approximate closely that of the theoretical composition, $Ca_2Mg_5(Si_4O_{11})_2F_2$.

(2) *Optical Properties*

The optical constants of selected single crystals of synthetic fluor-tremolite were measured at 23° C. with a petrographic microscope, using the oil immersion technique and monochromatic sodium (D) light. The results are compared with those of two natural hydroxy-tremolites (8), (9) in Table 2.

For comparison, the indices of refraction of a fluor-tremolite similarly synthesized by Van Valkenburg and Pike (10) are given as $\alpha=1.58$ and $\gamma=1.61$, while "the extinction angle as measured parallel to the elongation is about 16°". This is in close agreement with the present results.

The synthetic fluor-tremolite crystals obtained by Van Valkenburg and Pike, although acicular, appeared quite brittle. This observation was confirmed by the present authors. It is possible that the brittleness may be due to the comparatively large cross-sectional area of the synthetic fluor-tremolite crystals in relation to the natural asbestiform material.

TABLE 2. TREMOLITE OPTICAL CONSTANTS*

	Synthetic Fluor-tremolite	Natural Hydroxy-tremolite (8)	Natural Hydroxy-tremolite (9)‡
α	1.581 ± 0.001†	1.599	1.602
β	1.593 ± 0.002	1.613	1.618
γ	1.602 ± 0.002	1.625	1.631
$Z\wedge c$	21°	18°	16°
2V	$86\frac{1}{2}$°†	88°	82°±2°
Optical character	Biaxial negative	Biaxial negative	Biaxial negative

* Determinations on fluor-tremolite made by M. V. Denny.

† α and 2V determined by means of a 5-axis universal stage, using sodium (D) light.

‡ Analysis by Allen and Clement (reference (9), p. 414) shows presence of 1.21% Al_2O_3 and 0.6% alkali, plus small amounts of other impurities.

(3) *X-Ray Data*

The authors were able to find but scant information on the indexing of *x*-ray patterns of synthetic fluor-amphibole. The few *x*-ray investigations conducted apparently have been limited to comparing the location and intensities of the powder pattern maxima with those of a natural amphibole.

The most detailed *x*-ray data available on synthetic fluor-amphiboles are those given by Comeforo and Eitel (11), although no cell dimensions are reported. In the present study, accurate unit cell dimensions have been determined, and the *x*-ray pattern has been extended by a calculation of all Miller indices permissible by the space group symmetry of the tremolite structure ($C2/m$) up to 76°2θ. Every resolved peak in this range on a powder pattern has been indexed (see Table 3).

All powder-pattern maxima were determined with a Philips high-angle *x*-ray diffractometer, using unfiltered Cu radiation. The unit cell dimen-

Table 3. *X*-ray Diffraction Data (Powder) for Synthetic Fluor-tremolite (Space Group $C2/m$)

hkl	2θ obs.	2θ calc.*	Δ2θ	Meas. Int.
020	9.80°	9.815°	+0.015°	9
110	10.555	10.545	−0.01	>>100
130	17.465	17.48	+0.015	7
$11\bar{1}$	18.255	18.235	−0.02	5
200	18.72	18.725	+0.005	6
040	19.705	19.705	0	12
220	21.195	21.185	−0.01	25
$13\bar{1}$	22.98	23.00	+0.02	3
131 041	26.37	26.38 26.385	—	6
240	27.315	27.315	0	23
310	28.72	28.69	−0.03	>100
$15\bar{1}$ 221	30.44	30.43 30.44	—	8
330	32.025	32.01	−0.015	26
$33\bar{1}$	32.92	32.935	+0.015	3
151	33.12	33.14	+0.02	9
061	34.65	34.655	+0.005	2
$20\bar{2}$	35.51	35.53	+0.02	2
350	37.88	37.87	−0.01	4
$35\bar{1}$	38.68	38.675	−0.005	5
$42\bar{1}$	39.00	38.99	−0.01	5
$17\bar{1}$	39.28	39.27	−0.01	3
$31\bar{2}$	39.79	39.77	−0.02	1
171	41.45	41.455	+0.005	1
261	41.84	41.835	−0.005	4
202	44.36	44.34	−0.02	1
351	45.03	45.025	−0.005	4
370	45.43	45.445	+0.015	5
510	48.29	48.28	−0.01	5
242	48.935	48.95	+0.015	7
530	50.485	50.495	+0.01	4
461	55.835	55.835	0	18
480	56.365	56.355	−0.01	3
1·11·0	57.045	57.045	0	2
600	58.43	58.43	0	4
$15\bar{3}$	58.57	58.57	0	1
570 $35\bar{3}$	60.66	60.675 60.685	—	2
0·12·0	61.755	61.77	+0.015	8

TABLE 3—*Continued*

hkl	2θ obs.	2θ calc.*	$\Delta 2\theta$	Meas. Int.
551 48$\bar{2}$	61.93	61.94 61.96	—	2
3·11·0	64.005	64.02	+0.015	2
66$\bar{1}$	65.165	65.16	−0.005	6
512	68.91	68.92	+0.01	4
710	69.63	69.615	−0.015	2
263	70.695	70.69	−0.005	1
11$\bar{4}$	72.39	72.41	+0.02	2
22$\bar{4}$ 75$\bar{1}$	72.49	72.495 72.505	—	2
2·12·$\bar{2}$	73.325	73.33	+0.005	1

* Using $\lambda \mathrm{CuK}\alpha_1 = 1.54050$ Å.

sions were obtained by employing a fixed-time counting operation in conjunction with this instrument. The region surrounding a maximum was manually scanned down-scale, with intensity counts being made at decrements of 0.01° 2θ. The scanning operation was repeated five times in each case, the values then being averaged and plotted againts 2θ. The position of a maximum was read from a curve drawn through the plotted points. The instrumental setting used was the following: scale factor, 4-32 (depending on peak height); multiplier, 1.0 (thus the counting rate ranged from 200 to 1600 counts per second, full scale); time constant, 4 seconds; Geiger overvoltage, 300 volts; divergence slit, 1°; receiving slit, 0.003 inch; scatter slit, 1°.

The powder diffraction measurements were made using −200 +325 mesh powder, packed in the normal rectangular aluminum holder supplied with the instrument. For calibration purposes, appropriate peaks on a silicon standard compact (also supplied with the instrument) were determined before and after each fluor-tremolite reading, and the proper correction was applied. Such corrections, obtained by comparison with Parrish's (12) data for silicon, ranged from +0.005° to +0.012°. Thus, a value of 2θ to the third decimal place (the last place being somewhat uncertain) was determined for each of the maxima involved in the evaluation of the cell dimensions. The four peaks used in this determination were $600\alpha_1$, $0\cdot 12\cdot 0\alpha_1$, $461\alpha_1$, and $66\bar{1}\alpha_1$. The 2θ positions determined for these peaks and the resulting cell dimensions are given in Table 4, together with the calculated density.

Table 5 compares the unit cell dimensions obtained for synthetic

TABLE 4. MONOCLINIC CELL DIMENSIONS OF SYNTHETIC FLUOR-TREMOLITE

Peak	Determined 2θ	Cell Dimensions (Angstroms)
$600\alpha_1$*	58.431°	$d_{100}= 9.469\pm0.002$; $a_0= 9.781\pm0.005$
$0\cdot12\cdot0\alpha_1$	61.769°	$d_{010}=18.007\pm0.004$; $b_0=18.007\pm0.004$
$461\alpha_1$	55.834°	$d_{001}= 5.099\pm0.004$; $c_0= 5.267\pm0.006$
$66\bar{1}\alpha_1$	65.161°	$\beta=75°29'\pm5'=75.48\pm0.08°$
		Calculated density$=3.021\pm0.006$ gm./cm.^{3}†

* λCuKα_1 taken as 1.54050 Å.

† This compares with the measured density of 3.023 ± 0.006 gm./cm.^{3} at 20° C., as determined pycnometrically by M. V. Denny.

fluor-tremolite with Warren's (13) data on natural hydroxy-tremolite. It is interesting to note that substitution of fluoride for hydroxyl causes virtually no change in the a and c dimensions; b_0 increases slightly (1+%) while β increases by 1.5° (2%).

TABLE 5. TREMOLITE CELL DIMENSION COMPARISON

	Warren	Comeforo and Kohn	Increase
a_0	9.78 Å	9.781 Å	—
b_0	17.8	18.007	1+%
c_0	5.26	5.267	—
β	73°58′	75°29′	2%

The determination of the observed 2θ values listed in Table 3 was made using a chart operation with the Philips unit. The instrument setting was the same, except that the scale factor was constant at 16 (giving a counting rate of 800 counts per second, full scale). Additionally, the scanning speed was $\frac{1}{4}$° per minute and the chart scale $\frac{1}{2}$ inch per degree. With the aid of a binocular microscope (low power), the positions of the maxima were read to 0.005° 2θ (0.0025 inch on the chart). Following the method of Donnay and Donnay (14), the reading was ". . . taken at the mid-point of the peak width at approximately two-thirds of the peak height, an empirically determined value, which minimizes the interference of the α_2 peak and the effect of the detailed shape of the graph."

A chart was obtained, using the silicon standard compact, both before and after the analysis of fluor-tremolite. The corrections applied, forming a smooth-curve variation with 2θ, ranged from +0.035° to +0.06°. Referring to Table 3, listing only resolved peaks or doublets warranting mention, only one peak (310), which "ran off the chart," shows a deviation ($\Delta 2\theta$) of more than 0.02°. For all intents and purposes, the total of the positive deviations cancels that of the negative deviations, an additional fact speaking for the accuracy of the cell dimensions used in the calculations.

Single-crystal *x*-ray exposures (rotation and Weissenberg) were made both as a check on crystal quality and as a means for comparing intensity maxima and thus making an unambiguous indexing of certain peaks. Rotation, zero-, first-, and second-level exposures were obtained with rotation about the *c* axis. The rotation film yielded an identity period (c_0) of 5.3 Å, which, upon applying the calculated β of 75°29′, led to a d_{001} value of 5.1 Å. The zero-level Weissenberg film yielded directly 18.0 Å and 9.5 Å for d_{010} and d_{100}, respectively.

A check on the unit cell dimensions obtained from the *x*-ray powder pattern was sought by measuring on the optical goniometer the best synthetic fluor-tremolite crystals available (see Fig. 1). Six crystals were measured. All but one showed good to excellent unit prism faces. Front and side pinacoids were poorly developed but occasionally measurable. One crystal, twinned on (100), was found to be definitely terminated, the twinning giving rise to two basal pinacoids as the terminating faces. Indications of terminal faces were seen on another crystal, but these were too faint to measure. Several of the crystals examined showed indications of modified prism faces.

The interfacial angle $(100)\wedge(110)$ was determined, using 10 measurements on 5 different crystals. The readings ranged from 27°33′ to 27°44′, averaging 27°39′. The theoretical value, based on the ratio $d_{100}:d_{010}$ is 27°44′ ($\Delta = 5'$). The twinned crystal mentioned above permitted two direct measurements of β. The observed values were 75°11′ and 75°32′, averaging 75°22′. The calculated value for β is 75°29′ ($\Delta = 7'$). The agreement in these cases is considered good.

ACKNOWLEDGMENTS

The writers are indebted to Prof. Wilhelm Eitel, whose earlier work on the indexing of tremolites served as a starting point for the present investigation. Dr. Eitel also placed at our disposal translations of several of the articles discussed. Dr. R. A. Hatch made available data on the reactivity of fluor-silicate batches, offered helpful suggestions for the synthesis of single crystals of fluor-tremolite, and critically reviewed the manuscript. We are grateful to M. V. Denny for the optical and density determinations and to H. R. Shell and R. L. Craig for the chemical analyses. Mrs. G. M. Huff performed much of the calculating required for indexing the *x*-ray patterns.

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PETROGRAPHY OF THE TROCTOLITE OF THE WICHITA MOUNTAINS, OKLAHOMA*

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Abstract

This paper presents a detailed description of the petrographic nature of the pre-Cambrian troctolite of the Wichita Mountains, Oklahoma. The troctolites are composed essentially of bytownite (An_{75}), olivine, Fo_{75-80}, small amounts of diallage, hypersthene, and many accessory and secondary minerals. Development of coronas about olivine and plagioclase is described. The presence of spinel (pleonaste) in troctolite and sillimanite in the associated anorthosite indicates assimilation of aluminous material. The magma had a temperature somewhat above 1100° C. at the time of intrusion as evidenced by the occurrence of diopsidic lamellae in hypersthene.

Introduction

Though early in 1899, Vaughan (p. 47–48) reported troctolite in Iron Mountain of the Wichita Mountain System, Oklahoma, the rock has been neglected in subsequent investigations except for brief petrographic notes by Chase (1950), and a petrofabric study by Huang and Merritt (1952).

Field work was carried on during the academic years of 1949–1950, and 1950–51, when all outcrops of troctolite were studied and extensive collections made. The microscopic examinations of representative sections occupied the academic year of 1951–52. It is hoped that the present study may contribute to the petrographic and related character of the troctolite problem, and may shed light for the future investigation of the igneous complex of the Wichita Mountains.

The writers wish to express their appreciation to Gerald W. Chase of the Oklahoma Geological Survey for discussions on the troctolite problem and permission to use his unpublished geologic map of the Raggedy Mountains, Wichita Mountain System, Oklahoma, and for the loan of several thin sections of the rock under investigation.

Field Occurrence

The Wichita Mountains of southwest Oklahoma are composed of a series of pre-Cambrian igneous rocks, beginning with basic and ending with acidic composition. The troctolite is interpreted as formed by gravity settling of crystals as some outcrops show a downward gradation from an anorthosite through an olivine gabbro to a troctolite. Bands of anorthosite, feldspathic pyroxenite, pyroxenite, and diallagite may occur in any horizon of the basic rock series, while younger offshots of troctolite occurring as dikes also cut across the stratified igneous rocks. Except for the dikes, the boundaries between the rock types are indefinite, and there is always a gradual passage from one to another of the roughly horizontal layers.

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* Abstract of this paper by W. T. Huang under the title: "Petrography of the troctolite of the Wichita Mountains, Oklahoma, with remarks on preferred orientation of olivine crystals," was presented at the meeting of the Rocky Mountain Section of G.S.A. at Salt Lake City, Utah, May 8–10, 1952.

Though the base of the igneous complex is not exposed, it is believed that the mass attained a great thickness from data revealed by drilling on the flanks of the Wichitas. Also, the form of intrusion is conjectural, but it seems likely that it may have been a sheet or lopolithic body similar to the stratified gabbro-anorthosite and periodotite sheets of other parts of the world.

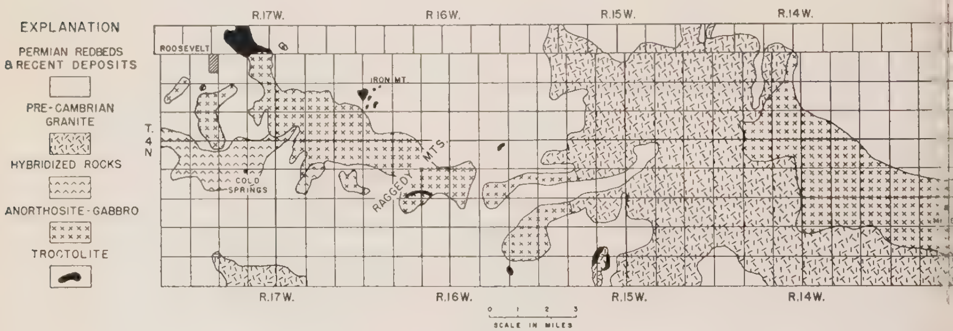

FIG. 1. Sketch map showing location of troctolite in the Wichita Mountains, Oklahoma.

Most troctolites occurring at the lower portion of this rock series crop out as scattered low hills near Roosevelt and other vicinities of the Raggedy Mountains (Fig. 1). Small sporadic outcrops also occur near Meers in the eastern Wichitas. Some outcrops are inliers surrounded by Permian Red Beds; others underlie granite, and still others underlie gabbroic rocks and anorthosite. One troctolite dike attains almost one mile in length and 150 feet in thickness. Small aplitic and pegmatitic dikes, not always mapable, cut across the troctolite outcrops. Within the troctolite exposures are many small local gradations into other rock types. For example, north of Roosevelt, the troctolite, with gradual decrease of olivine, laterally changes to olivine gabbro, which with absence of olivine, passes into labradorite and bytownite gabbros; in Iron Mountain a concentration of iron ores gives magnetite gabbro, which appears as an iron-rich differentiate.

Textures of troctolite range from medium to coarse-grained with feldspar tablets as much as 5.2 cm. in length and 3 cm. in width, and with olivine crystals as large as 4 cm. in diameter, the average grain size being about 4 mm. by 3 mm. Some phases show mafic minerals which form interstitial grains between blocky plagioclase crystals. Others, generally medium grained and relatively high in olivine crystals, are markedly saccharoidal. Olivine is evenly distributed in the rock, but local concentration is common. It is commonly altered to iron minerals, which stand out on the surface of the outcrop. Marked irregularities in grain size, some zonal arrangement of minerals in the coarsest phases, and occurrence of massive mafic minerals suggest that at least a part of the excessively coarse-grained material is pegmatoid in character.

In the Cold Springs area of the Wichita Mountains, Walper (1951, p. 51) described the gabbro-anorthosite as having a structure similar to schistosity and he ascribed it to magmatic flow. The banding of the troctolite is commonly conspicuous. Locally well-defined platy and linear parallelism of feldspar in the plane of the banding, were observed in several horizons. The bands, usually only a few cms. in thickness, continue with regularity for a few yards before they terminate by lensing out, or displacement by small faults. The contacts between adjacent bands are relatively sharp in some cases, and gradational in others. Within many of the bands there is a variation from an olivine-rich facies at the bottom to a feldspar-rich one at the top. Repetitions of this feature are common and reversals were observed. Hess (1938, p. 266) concluded that the factors responsible for primary banding in norite and gabbro are: (1) the relative density differences between each of the main constituents settling, plagioclase and pyroxene, compared to the density of the magma: (2) disturbance of the normal stage of quiescence in the magma by short epochs of gentle flow. This explanation is applied to the banding observed in some of the present igneous bodies in the Wichita Mountains by postulating that they were intruded in an approximately horizontal position, and were crystallized during the gentle magmatic flow. That the interpretation of the banding is the result of magmatic flow is further supported by local dimensional parallelism of the underformed plagioclase tablets in some places and by the tendency for elongated olivines to show dimensional parallelism in others.

PETROGRAPHIC NATURE OF THE ROCK

1. *Methods of feldspar determination*

Orthoclase was recognized and determined. The optical properties are as follows: $\alpha=1.514\pm0.002$, $\beta=1.518$, $\gamma=1.522\pm0.003$, $(-)2V=58°–62°$, plane of optic axes $\perp(010)$, plane of optic axes $\wedge(001)=4°$,

(010) ∧ (001) = 90°. These data are within the range of plutonic perthitic orthoclase as described by Spencer (1937, 1938).

The composition of the plagioclase was determined in each case by a combination of methods described by Winchell; especially valuable were extinction angles between Z or X and (001) or (010), in sections perpendicular to X and Z respectively (Winchell, 1951, p. 262). Selected sections were also examined with a universal stage, for the purpose of checking the composition of plagioclase (Turner, 1947). In all cases the composition of plagioclase as determined by the two methods agreed reasonably well; further, the axial angles of plagioclase as determined by the universal stage measurement were found to correspond closely with the curve given by Winchell (1951, fig. 148, p. 262).

TABLE 1. SELECTED MODAL ANALYSES OF THE TROCTOLITES, WICHITA MOUNTAINS, OKLAHOMA

	1	2	3	4*
Plagioclase	69.0	68.0	67.8	68.2
Olivine	26.0	29.8	26.4	26.8
Hypersthene	1.5	1.2	0.2	1.8
Diallage	1.5	1.0	1.1	0.5
Spinel	2.0	tr		1.5
Magnetite	tr	tr	4.5	1.2
Diopside	tr	tr		tr
Cummingtonite	tr		tr	tr
Lamprobolite	tr	tr	tr	tr
Hornblende	tr		tr	tr
Biotite	tr	tr	tr	
Muscovite	tr	tr		
Chrysotile	tr		tr	
Antigorite	tr	tr	tr	tr
Serpophite	tr	tr	tr	
Zircon	tr			tr
Apatite	tr	tr	tr	
Brookite		tr	tr	
Chromite	tr	tr	tr	tr
Ilmenite			tr	tr
Hematite	tr			tr
Range of anorthite content in plagioclase	70–75	76–78	72–74	72–75

tr = trace.

* Orthoclase and oligoclase occur in two sections.

1. One and one-half miles northeast of Roosevelt (SW¼, SW¼, Sec. 33, T. 5 N., R. 17 W.).
2. One mile northeast of Roosevelt (SE¼, Sec. 32, T. 5 N., R. 17 W.).
3. Iron Mountain (SE¼, NE¼, Sec. 12, T. 4 N., R. 17 W.).
4. 13 miles southeast of Roosevelt (NE¼, Sec. 9, T. 3 N., R. 15 W.).

2. *Detailed petrographic description*

Troctolites are holocrystalline, granular, medium-grained rocks, composed essentially of bytownite and olivine with diallage, hypersthene, minor accessories and secondary products. All the troctolites examined fall into Johannsen's family 2312P (1939, p. 225–226). Table 1 shows the selected modal analyses of the troctolites.

Plagioclase, generally lath-like, usually constitutes over half the volume percentage of the troctolite. Grains are occasionally very large, indicating a later pegmatitic development; otherwise, grain size averaging 4 mm.×3 mm., is comparable to the associated olivine. Occasionally the plagioclases occur as slender zonal laths, but most are unzoned, or occasionally as poikilitic crystals of more uniform composition. The laths were formed by crystallization in a magma undergoing movement. The unzoned and poikilitic habits are ascribed to crystallization in a quiescent magma. The zoned crystal has a core of An_{78} and mantle of An_{74}. Sharply defined zonings are wanting; the transition in composition from the core to the edge is commonly a gradual one. The total variation in composition is from $Ab_{30}An_{70}$ to $Ab_{22}An_{78}$, but the great majority falls in $Ab_{25}An_{75}$.

The plagioclases represented are bytownite. Twinning is universally developed, and twinning laws were determined with the migration curves (Turner, 1947). Relative abundance of plagioclase twinning laws is indicated in Table 2. In general, the more calcic plagioclases tend to twin according to the so-called less common laws. Albite law is universally present.

TABLE 2. RELATIVE ABUNDANCE OF PLAGIOCLASE TWINNING LAWS

Twinning Laws with Anorthite Content			Relative Abundance
Normal twin law:	Albite	An_{25-38}	Abundant
		An_{70-78}	Abundant
Parallel laws:	Ala B	An_{25}	Rare
	Carlsbad	An_{72}	Present
	Pericline	An_{72-75}	Present
	Acline	An_{78}	Rare
Complex laws:	Albite-Carlsbad	An_{76}	Present
	Albite-Ala	An_{78}	Rare

Remark: sodic plagioclases, An_{25-38}, were introduced.

Well developed dust-like and needle-shaped magnetite enclosures were seen in plagioclase. The needles occupy the center of the crystals;

the exterior of the crystals is generally free from inclusions. Not infrequently, the acicular bodies are altogether absent, and then the minute dots are arranged in lines which indicate the position of the twinning lammelae, twinning planes, and cleavages. Pseudo-zonal structure is occasionally produced by inclusions. Fine reddish brown rods, possibly hematite, trending parallel to the intergrowth planes of the lamellae were observed. Zircon and apatite appear as inclusions; while long apatite needles, too long to be entirely enclosed, intersect the plagioclases. Olivine is rarely enclosed, possibly because it invariably occurs in large crystals.

Evidences of syncrystalline deformation are absent and the plagioclases are usually fresh. Alteration when present is restricted to the incipient development of clayey minerals too small to permit identification. The feldspar is also patchily replaced by the invading serpentine.

Orthoclase and sodic plagioclase, An_{25-38}, occur in small quantities in the troctolite collected from outcrops, 13 miles southeast of Roosevelt. It is believed that they were introduced by contamination of the adjacent granitic rocks in a manner similar to that leading to the formation of granodiorite and other hybrids in the Wichita Mountains (Walper, 1951).

Olivine is the second most abundant mineral in the troctolite; it never shows a well-defined crystal nor it is corroded. The olivine also occurs in ramifying and wormy shapes giving the rock an ophitic-like texture. In size it varies from 0.8 mm. to 3.4 mm., and it is colorless to a greenish tint in thin section; it has an imperfect cleavage parallel to (100). In some olivines this plane of mechanical weakness is well shown by the presence of minute rod-like opaque and semi-opaque schiller inclusions, which tend to sharply orient in (100) of the host crystal. Twinned olivine was also noted.

The olivine is partly older, but mostly contemporaneous with plagioclase, and always older than the pyroxenes, for the latter commonly surrounds it.

The olivines were determined with the curves of Winchell (1951, p. 500–501). Optical properties are shown in Table 3.

Over 75 per cent of all determinations fall in Fo_{75-80}, and no exceptional relations are shown by the composition of the olivines in the troctolite. Generally, the olivines show a slight range in composition within one thin section, though individual crystals are of uniform composition.

Zoning of olivines was observed only in two slides from an outcrop one mile northeast of Roosevelt. The zoned olivines are surrounded by numerous minute granules of olivine. According to Walker and Polder-

TABLE 3. OPTICAL DATA ON OLIVINES

Specimen Number 2V and Optic Sign	Beta Index	Per Cent Forsterite
H24 (+)83°	1.662	96
H31 (+)84°	1.682	92
H36 (−)87°	1.694	89
H45 (−)87°	1.698	80
H28 (−)86°	1.710	75
H37 (−)81°	1.712	70

vaart (1949, p. 663), the zoning is ascribed to a local acceleration in the crystallization of olivine, presumably caused by magmatic reaction with a quartzite xenolith. Though not conclusive in the present case, it is strongly supported by the widespread occurrence of the stoped material, both igneous and sediments of various composition in the Wichita Mountains igneous complex. The scarcity of the zoned olivines may be due to alteration of the crystals, destroying any evidence of the phenomenon.

Feathery reaction rims are developed sporadically between the olivine and plagioclase. Some olivines are surrounded by coronas built against anhedra of plagioclase feldspar, and the olivine is forsterite in composition. The reaction minerals are small; few grains are larger than 0.1 mm. The reaction products are composed of two shells. Close to olivine occurs a shell, approximately 0.07 mm. in width, of pinkish hypersthene; this shell passes outward into a second shell commonly 0.2 mm. in width, composed of minute dark grains. The shell appears cloudy in many places. The small grains prevent precise determination, but the mineral has the optical properties of a diopsidic-spinel symplektite (Fig. 2).

Another type of corona was recognized. The kelyphite of greenish amphibole prisms (hornblende), commonly 0.1 mm. in width, is almost continuous, and it has a uniform width indicating that the amphibole rim was formed largely from olivine. Spinel rarely appears in this rim. It is logical to consider that the amphibole was formed from the original olivine grain just as the diopside-spinel symplektite replaced plagioclase.

The contact between plagioclase and iron ore is marked by a corona, especially when the ores are large in size. The reaction product appears to be greenish amphibole prisms so small and so closely packed, that precise identification is difficult (Fig. 3). The coronas between plagioclase and iron ore were originally formed between plagioclase and olivine that was selectively replaced by iron ore; for incomplete replacement of olivine by iron ore can be clearly recognized. A similar description is given by Sclar (1951, p. 1477). Thus some iron ores are late in development.

Coronas are an intriguing feature of many basic rocks (Buddington, 1930, p. 290). In his recent studies of the coronas and coronites, Shand (1945) concluded that the coronas are the result of thermal metamorphism, and that the instability of olivine, probably because of its tenor of iron, has caused the rims to form by a process of ionic migration. The troctolites of the Wichita Mountains contain olivines of Mg-rich variety as shown by optical properties (Table 3). Shand's conclusion that ferrous iron is important in corona formation is not supported by the troctolite in the Wichita Mountains. Osborne (1949, p. 94) believes that Shand's conclusion may help to explain the reaction rims formed against plagioclase and iron ores. The writers find their opinion irreconcilable with Osborne's explanation in the present corona-bearing troctolite. For, as already noted, olivines with corona structures were selectively replaced by late iron ore. Field evidence, from the corona-bearing troctolites in the Wichita Mountains, lends support to Shand's conclusion that thermal metamorphism acting upon rocks of suitable mineralogical composition, seems to offer the most likely solution for the corona problem, for the corona-bearing troctolites collected are commonly cut by pegmatitic dikes.

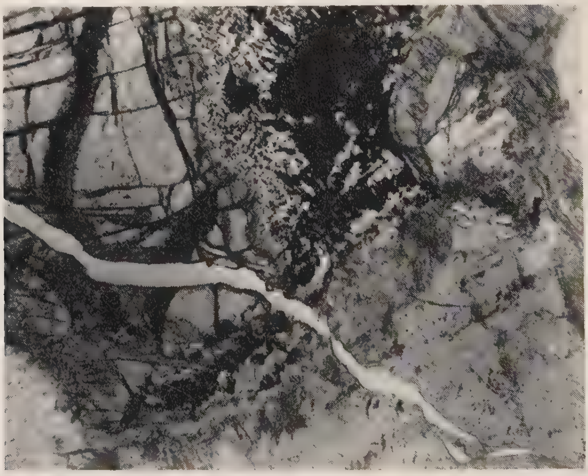

FIG. 2. C-142, plane light ×58. Olivine is surrounded by a corona built against anhedra of plagioclase An_{75}. The reaction products are composed of two shells. Close to the olivine is a shell of hypersthene. This shell passes outward to a diopside-spinel symplektite. Note a part of the olivine is selectively replaced by iron ore.

Location: One mile northeast of Roosevelt (SE¼, SE¼, Sec. 32, T. 5 N., R. 17 W.).

Olivine is the mafic mineral most susceptible to alteration. This is in the form of serpentinization, beginning along cleavage cracks and margins of the crystal, and always present to some degree. The serpentines are fibrous antigorite, chrysotile veinlets and isotropic serpophite. Coincident with this serpentinization are developments of ilmenite and magnetite.

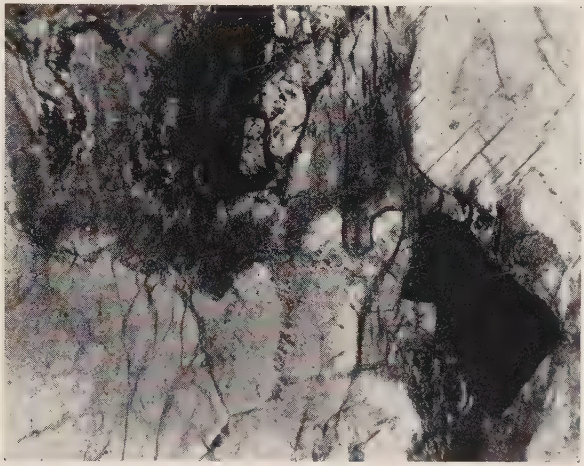

FIG. 3. C-164, plane light, ×58. In the upper left, olivine is surrounded by a kelyphite of greenish hornblende prisms, and is selectively replaced by iron ore. In the lower right, a corona is built about iron ore and plagioclase upon completion of replacement of olivine. Location: Thirteen miles southeast of Roosevelt (NE $\frac{1}{4}$, Sec. 9, T. 3 N., R. 15 W.).

Orthopyroxene, though in small quantities, presents an interesting petrographic study; it forms narrow shells from 0.02 mm. to 0.08 mm. in width, around the olivine grains, indicating a younger age than the olivine in the course of crystallization. Most orthopyroxenes, however, occur as oblong-shaped crystals which average about 0.2 mm. by 0.8 mm. in dimensions. The orthopyroxene was determined using Hess and Phillips' curve (1940). Optical properties of orthopyroxene are: $(-)2V=64°$, $\gamma=1.700\pm0.002$, faintly pleochroic: X = pinkish, Y = colorless, and Z = pale to greenish. These data indicate hypersthene with enstatite content $En_{73}Of_{27}$.

Some hypersthenes contain schiller inclusions, which are composed of fine needles arranged parallel to the *c*-axis, and of small plates of a reddish-brown color lying parallel to (010) or (110). The exact nature of these minute inclusions cannot be determined; the unusual high relief suggests brookite. Other hypersthenes are marked by lamellation, often parallel to (010), which at first suggests multiple twinning. The petrogenetic significance of this mineralogical feature will be discussed later.

The hypersthene is commonly fresh, but not infrequently shows alteration into various minerals. Serpentines not only fill the cleavage cracks of the hypersthene, but also those of the adjacent plagioclase, and occur as marginal films between the grains of those two minerals. The mineral is composed of fine fibers, which are characterized by weak pleochroism: X = greenish tint, Z = green, birefringence of about 0.01, and is most likely a variety of antigorite. The alteration of hypersthene not only produces serpentine minerals, but also develops magnetite grains.

Another interesting type of alteration of hypersthene is the production of cummingtonite. The process takes place along the cleavages and margins of the hypersthene. Commonly the alteration is incomplete, giving the impression of patchy intergrowth of the two minerals. In an advanced stage, the hypersthene changes to cummingtonite and greenish amphibole. The amphibole occurs along the margins, and was obviously formed as a reaction product between hypersthene and plagioclase in a manner similar to that described by Asklund (1925, p. 23). The cummingtonite borders both the hypersthene and the iron ore: the deepest brown cummingtonite is seen where the mineral is in contact with the hypersthene. The pleochroism of cummingtonite is: X = colorless to pale, Y = yellowish brown, and Z = chestnut brown. On the universal stage every crystal proved to be optically positive with $2V(+) = 82°–84°$ and a maximum extinction angle of 20°, indicating molecules of 64 per cent of grünerite $Fe_7Si_8O_{22}(OH)_2$ (Winchell, 1951, p. 428).

Alteration of hypersthene into cummingtonite has been recorded by several workers. Asklund (1925, p. 20–25) described it in a noritic gabbro in Stavajo at Kolmarden, and he listed a number of other authors. Lundegårdh (1943, p. 340) found similar alteration rims of colorless fibrous amphibole surrounding hypersthene remnants in the ultra-basic gabbro (hypersthene eucrites) in the Grovstanas region, Sweden, and agreed with Asklund's identification of cummingtonite. Heitanen (1947, p. 1042–1043) and N. F. M. Henry (referred by Stewart, 1947, p. 483) also describing the similar alteration and illustrating it by the following chemical equation:

$$7(Fe, Mg)SiO_3 + SiO_2 + H_2O \rightarrow H_2O(Fe, Mg)_7Si_8O_{24}$$
$$\text{7 Hypersthene} + \text{Quartz} + \text{Water} \rightarrow \text{Cummingtonite.}$$

In view of the intensive hydrothermal activity in the area studied, the above reaction can be equally applied to the present mineral alteration.

Lastly, the hypersthene is also altered to biotite. The brown mica wisps are intimately associated with hypersthene having marked pleochroism from brown to almost colorless, and with almost parallel extinction, thus differing from the cummingtonite.

Clinopyroxenes occur in small amounts in troctolite, but it increases in amount giving diallage gabbro. The clinopyroxene is rarely twinned; occasionally it is zoned. The presence of parting on both (100) and (001) in some of the mineral makes the variety name diallage appropriate. Clinopyroxene appears colorless throughout and is always optically positive, with the optical plane parallel to (010). The optical angle, extinction $Z \wedge c$, and beta refractive index were determined. The method of composition determination suggested by Hess (1949, p. 636) was used, i.e. the intersection of the beta value with the crystallization curve is a check on the composition inferred from 2V and the beta index. Table 4 shows the optical properties and composition of the clinopyroxenes in the troctolites. The petrologic significance of the composition of clinopyroxenes cannot be deduced, until the investigation of the basic igneous rocks of the Wichita Mountains is completed. It is hoped, however, that the present data may aid in the interpretation of the clinopyroxenes in the basic igneous rocks in that area.

TABLE 4. OPTICAL PROPERTIES AND CHEMICAL COMPOSITION OF CLINOPYROXENES

Nomenclature (after Hess, 1941)	2V	Beta Index*	$Z \wedge c$	Composition Inferred	Specimen
Augite	46° 53°	1.702 1.688	43° 46°	$Wo_{36}En_{37}Fs_{27}$ $Wo_{41}En_{44}Fs_{15}$	In troctolite outcrops near Roosevelt
Ferroaugite	45° 46°	1.721 1.724	52° 48°	$Wo_{27}En_{21}Fs_{52}$ $Wo_{31}En_{20}Fs_{49}$	Iron-rich differentiate in Iron Mountain

* The limits of error of the indices of refraction are 0.003.

Strongly pleochroic biotite, X = pale brown, Y = Z = reddish brown, occurs in small amounts. According to Hall (1941, p. 30), the red brown biotite is due to the high titania and low magnesia content: magnesia masks the color. Pleochroic lamprobolite, X = yellowish brown to Z = brown, was noticed in several slides. Muscovite threads occur in clusters, but in negligible amounts. Euhedral apatite crystals are invariably enclosed in olivine and plagioclase crystals. Chromite was recorded and commonly associated with magnetite in a fine granular habit; it is also seen in serpentinized olivine cracks and cleavages. Under the microscope, the center of the grains appears opaque and the edge translucent brown.

Primary ilmenite is practically absent from many slides in widely scattered outcrops, but it becomes increasingly prominent in some layers and in Iron Mountain. The crystals tend to be skeletal or idiomorphic, but are also intimately intergrown with magnetite crystals. Merritt (1939, p. 277–278), also observed the intergrowth of the magnetite and ilmenite in the iron ores of the Wichita Mountains. Examination of polished sections of these iron ores in reflected light reveals that the ilmenite consists of a typical exsolution intergrowth of lamellae of ilmenite, in the octahedral planes of magnetite. Some of the ilmenite lamellae are quite broad, but others can be detected with only high magnification. Diffusion and segregation of the ilmenite has led to a separation of irregular shaped areas of ilmenite at the margins of some of the magnetite crystals. According to Edwards (1938, p. 48–52), this indicates a moderately slow rate of cooling. The amounts of ilmenite vary considerably. In some cases, the mineral constitutes as much as 2 per cent of the rock.

Finally, considerable amounts of spinel were found in several slides in addition to those described in connection with the formation of corona The occurrence of this mineral bears an important petrogenetic significance, and it will be discussed in a later section.

3. *Petrogenetic significance of some mineralogical features*

Several mineralogical features have important petrogenetic significance. These are discussed as follows:

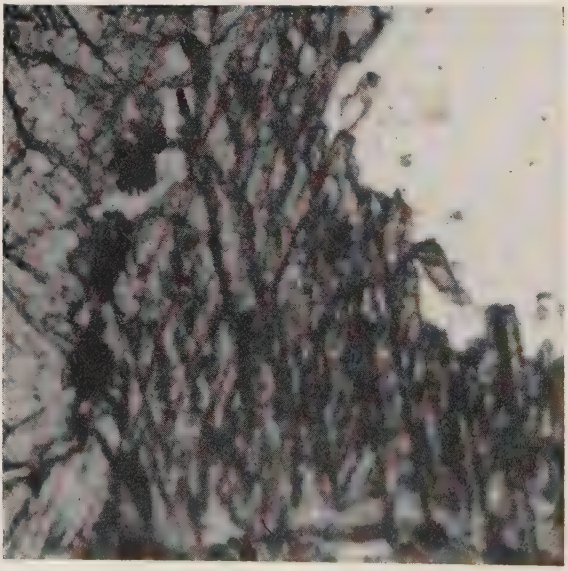

Fig. 4. H-36 plane light ×56. Intergrowth of diopsidic lamellae and hypersthene. Location: One mile northeast of Roosevelt (SE ¼, Sec. 32, T. 5 N., R. 17 W.).

First, some hypersthenes are marked by lamellation (Fig. 4) often parallel to (010), resembling multiple twinning. Such lamellation has, however, been considered by Hess and Phillips (1938) as due to inversion of pigeonite to orthopyroxene, with the segregation of diopside in the form of an intergrowth, orthopyroxene being able to hold $CaSiO_3$ in solution to the extent of about 9 per cent, but unmixed on further cooling. Hess further clarified the pigeonite and orthopyroxene stability relations in a diagram (1941, p. 583). In the present rocks where the lamellation is not continuous across the crystal, it has the appearance of an exsolution effect rather than one due to twinning. The lamellae have lower indices of refraction than the enclosing hypersthene, low birefringence and extinction angles 40°–46°. Measurements of this intergrowth on a universal stage was plotted in Fig. 5. The lamellae (En_{75}) are almost parallel to the parting plane (010) in the hypersthene. The optical angle of the hypersthene is of $(-)2V=64°$, while that in the lamellae was measured as $(+)2V=68.5°$. One of the optical axes of both minerals almost coincides.

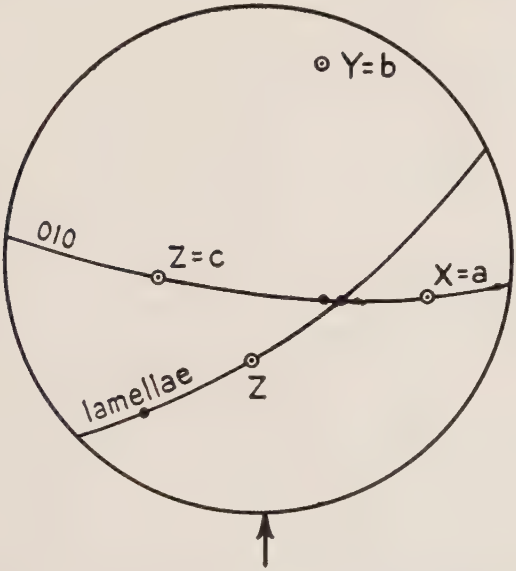

Fig. 5. Stereographic projections showing orientation of the optic axes and axial planes of the hypersthene and the diopside lamellae.

Edwards (1942, p. 587–590, 593–602) observed similar intergrowths of diopside and hypersthene in dolerites of Tasmania, and considered it as due to exsolution of clinopyroxene attending an inversion of pigeonite to hypersthene. Recent studies in the inversion of pigeonite to orthopyroxene by Walder and Poldervaart (1949, p. 635–638) in the Karroo dolerites, South Africa, confirm, and in part extend Hess's explanation.

The occurrence of these diopside lamellations gives a valuable geologic thermometer. The inversion temperature of pyroxene of this composition (En_{75}) has been determined experimentally as about 1100° C. (Hess, 1941, p. 582–583). The intergrowth of diopsidic lamellae in hypersthene found in the troctolite indicates that the magma had a temperature slightly above 1100° C. at the time of intrusion.

Second, troctolite and associated melanocratic rocks frequently contain small amounts of a brownish to vivid green spinel (pleonaste). Spinel was first noted in the melanocratic rocks collected two miles south of Roosevelt near Cold Springs area, where the stoped material and assimilation are most prominent (Walper, 1951). At first, it was believed that spinel represented excess Al_2O_3 thrown out in the process of metasomatism of xenoliths of aluminous sediments.

Later, spinel was found among the mafic constituents of the troctolite and associated rocks. This suggests that the spinel is rather a product of crystallization from a magma, or a result of unmixing during later stages of crystallization. Bowen (1928, p. 277, et seq.), discussed the reactive crystallization of spinel and showed that under certain conditions of falling temperature it would eventually disappear, but has been preserved in some rocks by envelopment in cloaks of silicates which has protected it from the surrounding magma. Bowen also pointed out that partial replacement by clinopyroxene might be expected with falling temperatures. In such circumstances, more or less complete coronas of spinel in contact with olivine might sometimes be expected, surrounded by other silicates without spinel. In the present troctolite, however, olivine may have disappeared through reaction and the spinel is scattered through the outer shell in dactylic growths. Some spinels are enclosed in olivine, others in clinopyroxene, and still others occur in the interstitial space between feldspars. It seems possible that much of it has been developed consequent to the reactive replacement by clinopyroxene of magma containing excess Al_2O_3. As already noted, the corona-bearing troctolites are commonly cut by pegmatitic dikes. Olivine is unstable in contact with alumina-rich hydrothermal solutions, and reacts metasomatically according to the following scheme (Barth, 1952, p. 329):

$$\begin{array}{c}(Mg, Fe)_2SiO_4 + Al_2O_3 \rightarrow (Mg, Fe)SiO_3 + MgAl_2O_4 \\ \text{olivine} + \text{alumina} \rightarrow \text{hypersthene} + \text{spinel.}\end{array}$$

When the spinel is enclosed in olivine, it is assumed that it has precipitated during decreasing temperature, and the olivine has protected the spinel from reaction. It should be stated that most spinels do not assume crystal forms, and the grains between feldspars are perhaps accidental inclusions. The foregoing discussions lead to the conception that the magma, or a portion of it, is abnormally rich in Al_2O_3, perhaps due to incorporation of aluminous sedimentary material at levels far below the present emplacement. A similar conclusion has been reached by Prider (1940, p. 378–379) in his studies on the constitution of the spinel-olivine-hypersthene xenoliths in granite gneisses from Toodyay, western Australia. That the magma is abnormally rich in Al_2O_3, is further supported by the occurrence of sillimanite in the associated anorthosite in the Wichita Mountains. There can be no doubt that the original sediments were aluminous, for the Meers quartzite now occurring as roof pendents (Taylor, 1915, p. 32; Hoffman, 1933, p. 31; Merritt 1948) in the eastern Wichita Mountains contains small amounts of sillimanite. The incorporation of older igneous country rocks, widespread occurrence of stoped igneous materials, metasomatism and transfusions of quartzitic sediments are common phenomena in the Wichita Mountains igneous complex. Whether the feeble development of muscovite in the troctolite, and in the associated gabbro and anorthosite throughout the Wichita Mountains, represents an arkosic element in the sediments is a matter of further research. The apparently sporadic nature of the development of spinel, too, needs further consideration, though it may be explained by irregular distribution of aluminous stoped sediments, followed by convection and restrained diffusion.

The presence of some aqueous fluids throughout much of the igneous cycle, is evident because of the presence of muscovite, biotite, and lamprobolite in the troctolite and melanocratic rocks. Some of the fluids may have been provided by sedimentary xenoliths absorbed by the magma.

Finally, several of the troctolites are characterized by ideal reaction groupings. Even in those corona structures, isolated crystals of the minerals forming the coronas are usually found sporadically among the feldspars. Not infrequently the mafic minerals are present in well-defined clots composed of various minerals. The association is apparently random, and there is no indication of reaction zoning in mafic mineral aggregates.

The reaction zoning is in accordance with Bowen's reaction principle. Starting with the core minerals with successive zones to the right, the following groups were noticed:

1. Olivine———hypersthene———amphibole with spinel.
2. Hypersthene———diopside———hornblende———magnetite.
3. Hypersthene with a little spinel———diopside with spinel.
4. Hypersthene———biotite.
5. Iron-ore———hornblende

It is clear that during the magmatic stages of crystallization, concentration of potash in the magma was low in the troctolite, and biotite appears as an end member of the reactions. Potash in excess of that in a normal troctolite magma must have been present, as it is evidenced by the sporadic and minute muscovite in the rock.

Summary and Conclusions

Field occurrence of the rock types, leucocratic on the higher parts, and melanocratic in the lower parts of many outcrops and at the apparent base of the intrusion in the Wichita Mountains, Oklahoma, strongly suggests that development to a great extent is due to gravitational differentiation. The troctolite facies of the basic igneous rocks is produced by accumulation of olivine crystals by gravity settling. Other petrologic features such as the indication of incorporation of quartzite xenolith, banding of the rocks, and occurrence of the spinel in several rocks, demand the invocation of other petrogenetic factors.

The troctolites are composed essentially of bytownite, An_{75} and olivine, Fo_{75-80}, with small amounts of diallage, hypersthene, and many accessory and secondary minerals. The formation of corona-bearing troctolite accords with Shand's conclusions, i.e. due to instability of olivine under thermal metamorphism, though Shand's conclusion that ferrous iron is important in corona formation is not supported by the present study. The occurrence of diopside lamellae in hypersthene indicates that the magma had a temperature slightly over 1100° C. at the time of intrusion. Two kinds of feldspars are present in the troctolites: namely, calcic plagioclase An_{70-78} and orthoclase accompanying sodic plagioclase An_{25-38}. The bytownite is primary whereas the latter is introduced by contamination from adjacent granitic rocks.

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SOME HYPERSTHENES FROM SOUTHEASTERN PENNSYLVANIA AND DELAWARE*

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ABSTRACT

A new procedure is proposed for the chemical analysis of minerals high in iron, magnesium and silica; and low in calcium, aluminum and the alkalies. Chemical, optical, x-ray and spectrographic analyses of 8 high iron hypersthenes from Southeastern Pennsylvania and Delaware are presented. Curves are given showing the variation of the optical properties with chemical composition.

INTRODUCTION

In general, although optical properties of minerals depend on their chemical composition, mineralogists have usually been content to put all their effort into obtaining the optical properties while letting someone else make a mediocre chemical analysis of the mineral. While it is true that the mineralogist, in most cases, cannot be expected to do the analysis himself, he should see that it is done well.

A recent investigation (1, 2), as to the reliability of results of analysis of silicate rocks, has shown that even when performed by experts, the results obtained varied widely. This is no reflection on the analysts, but only proves that silicate analyses are difficult.

In the case of the analysis of a mineral, another complication arises. Most laboratories simply follow Washington's method of analysis (3). Yet the composition of the mineral being analyzed is usually completely different from that of a rock for which the method was designed. For instances, in a high iron hypersthene, very little calcium, aluminum, sodium and potassium are present, while rocks contain relatively large amounts of all four. Magnesium and ferrous iron amount to about 50 per cent of the total in a hypersthene, whereas these same elements are generally contained in very small amounts in a rock. Consequently, the usual method of rock analysis should not be used and a new method devised.

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This paper proposes a method for the analysis of high iron hypersthenes and any similar material. In the same category might be included the entire enstatite-hypersthene series, the anthophylites and the olivines; that is, any mineral containing high iron or magnesium, high silica, and very low calcium, aluminum and alkalies.

Previous work on the analysis of minerals has usually been done on crystals which were large enough to be hand picked and separated. Except for the work of Hess and Phillips (4) and Hess (5), very little attention has been given to minerals from fine grained rocks. This has been due to the difficulty of separating the minerals from the rock. However, with the advent of the Franz isodynamic magnetic separator, fine grained rocks can be separated into their components fairly easily. These fine grained minerals give a truer picture of the relation of the mineral to the rock than large size crystals which had to form under special conditions. At the same time, a much larger amount of pure mineral can be obtained, allowing the analyst much more freedom in his work.

Another fault of many analyses of minerals has been the lack of purity of the material analyzed. While optical data can be obtained on impure material simply by picking out the correct grains to measure, the chemical analysis should be made on a sample having a purity of over 99 per cent. Otherwise, the chemical analysis can have little meaning, since the effect of the impurities on the analysis can not be determined. Yet many curves have been drawn using analyses of impure minerals. It is paradoxical that mineralogists will refuse to accept a chemical analysis that is over one half per cent in error and yet submit for the analysis a mineral with 5 per cent impurity. If the mineralogist demands a 99 per cent accurate analysis, he should submit a 99 per cent pure sample.

This study has been concerned with the separation and analysis of high iron hypersthenes from a series of rocks found in southeastern Pennsylvania and Delaware. The rock sites concerned are the Wilmington gabbro massif, the Baltimore gneiss complex and ultrabasic rocks associated with them and with the Wissahickon schist. This is part of a major study of the rocks and their relationship throughout this region, being carried out by the Geology Department of Bryn Mawr College. At the time of the separation of the hypersthenes a series of hornblendes from the same and associated rocks were separated and analyzed. This work will be reported in a separate paper by Abraham Rosenzweig of Bryn Mawr College.

In every case, the material taken for analysis was obtained in a purity of over 99.5 per cent. No correction was made for the impurity, since this degree of purity is as good as the accuracy of the chemical analysis. The purification was accomplished by means of a Franz isodynamic magnetic separator and heavy liquids. Enough material was obtained in pure form to carry out complete chemical and optical analyses on each sample. In no case was a single crystal analyzed, but the material was always obtained from relatively fine grained rocks.

Much work has been done previously on this series of minerals, notably by Winchell, Walls, Henry and Poldervaart; relating the chemical composition to the optical properties. However, there are questionable points in all of this work. The first curves drawn for the hypersthenes were by Winchell in 1923 (6), and were used as standards for years when published in his text (7). However, because of the lack of complete data and the possible inaccuracy of some analyses, the curves were not too reliable. He made the statement that "the curves were not final and infallible but the best from all available data" (6). The data used was collected from the literature. Practically all the analyses had been made on single crystals, hand picked by the mineralogists.

The next major attempt at drawing curves for this series was done by Walls (8) and Henry (9), working about the same time. They did some original work on material purified by them but the majority of the points on which they based their curves were the same as those used by Winchell and suffered from the same faults. Even the material analyzed by them was not of the highest purity. For this reason Walls states " . . . it is clear that no high degree of accuracy can be claimed for these curves."

The curves obtained by Hess and Phillips (4) were the first based on analyses which had been done with great care, on pure material, and on material from fine grained rocks. Where the material analyzed was impure, the impurity was analyzed and corrections made for it. From this careful work very good curves were obtained. However, no hypersthene containing over 25 per cent ferrous silicate was included.

In 1947 Poldervaart (10) described the analyses of two hypersthenes and drew curves based on most of the preceding work. Winchell, in the latest edition of his text (11), has published a new series of curves, for which he gives no reference but which resemble those of Poldervaart. Still, these curves are based on analyses which are not of the highest reliability. Therefore, it was proposed to analyze the pure high iron hypersthenes obtained from the fine grained rocks in this region and use this data as a basis for a group of new curves.

LOCATION AND DESCRIPTION OF THE HYPERSTHENE-BEARING ROCKS

Sample 35-5. This specimen was found 0.1 mile north of the crossroads of U. S. Route 202 at Talleyville, Delaware, 300 yards west of the road (West Chester 92756).* It is a noritic eucrite of medium fine grain. By volume analysis on a thin section it contains: 10 per cent hypersthene, 6 per cent augite, 23 per cent hornblende, 2 per cent magnetite and 59 per cent plagioclase of composition anorthite 72 per cent. There is a trace of apatite.

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* Note: This system of location is based upon the standard 15-minute quadrangles of the United States Geological Survey, which are subdivided into nine 5-minute sub-quad-

Sample 35-6. This specimen came from an outcrop in the park at Franklin and Sycamore Streets, Wilmington, Delaware (Wilmington 31268). It is a quartz norite: dark, massive and fine-grained. By volume analysis it contains: 11 per cent hypersthene, 7 per cent augite, 14 per cent hornblende, 5 per cent magnetite, 13 per cent quartz and 50 per cent plagioclase of composition anorthite 58 per cent. There is a trace of apatite.

Sample 35-8. This specimen was found in an abandoned quarry on the east bank of Brandywine Creek in the city of Wilmington, Delaware (Wilmington 32237). It is a quartz norite, dark and of fine grain and is the prevailing type in the quarry. By volume analysis it contains: 5 per cent hypersthene, 1 per cent augite, 3 per cent magnetite, 27 per cent quartz and 64 per cent plagioclase of composition anorthite 46 per cent. There is a trace of apatite and biotite.

Sample 35-9. This specimen was found in the same quarry as sample 35-8 but cross-cutting the prevailing rock as dikes. It is a norite of fine grain, slightly darker than 35-8. By volume analysis it contains: 18 per cent hypersthene, 19 percent augite, 3 per cent magnetite and 60 per cent plagioclase of composition anorthite 52 per cent. There is a trace of apatite and epidote.

Sample 35-13. This sample was found in Radnor quarry, in the lower quarry wall on the west side (Norristown 85826). It is an altered hypersthene gabbro of medium grain. By volume analysis it contains: 14 per cent hypersthene, 14 per cent augite, 4 per cent magnetite, 6 per cent potash feldspar, 7 per cent garnet and 55 per cent plagioclase of anorthite content 41 per cent. There is some anti-perthite and sericite with a little apatite and epidote.

Sample 35-14. This specimen was also found in Radnor Quarry (Norristown 85826), but in the northwest corner. It is a hybridized norite, of coarse grain. By volume analysis it contains: 10 per cent hypersthene, 3 per cent magnetite, 26 per cent quartz, 4 per cent potash feldspar and 57 per cent plagioclase of composition anorthite 36 per cent. There is some anti-perthite and sericite and traces of garnet, biotite and apatite.

Sample 35-19. This specimen was found in a boulder fence on the south side of Faulk Road, 1.5 miles northeast of the intersection of U. S. Route 202 (West Chester 96413). It is a norite, medium grained and fairly light in color. By volume analysis it contains: 21 per cent hypersthene, 9 per cent augite, 13 per cent hornblende and 57 per cent plagioclase of composition anorthite 69 per cent. There is a trace of magnetite.

Sample 35-32. This specimen was found in boulders in a field 800 feet south of the West Chester Pike at the Dinwoody Home (Chester 22476). It is a eucritic norite of coarse grain. By volume analysis it contains: 55 per cent hypersthene, 10 per cent augite, 1 per cent hornblende and 34 per cent plagioclase of composition anorthite 83 per cent. There is a trace of magnetite.

Preparation and Purification of Samples

The rock was crushed by means of jaw crushers and steel rolls, so that grinding action was avoided as much as possible to prevent oxidation of

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rangles. These sub-quadrangles are number 1 to 9 from left to right. The first number in the designation denotes this 5-minute sub-quadrangle. Each sub-quadrangle is then subdivided into 9 parts similarly, which are denoted by the second number in the designation. These are similarly subdivided and designated, so that with five numbers a location is very accurately placed on the map.

the ferrous iron. The crushed material was screened, and that portion passing through the 100 mesh screen and remaining on the 150 mesh screen was taken for the separation. This material was washed with water to remove adhering fines and dried.

Impure hypersthene was separated from the other minerals in the rock, such as magnetite, augite, hornblende, quartz, and feldspar, etc. by means of a Franz isodynamic magnetic separator. Product purity by this method was between 95 and 99 per cent. The sample was washed with water to remove any fines formed during the separation and then dried. Hypersthene was separated as the heavy fraction with methylene iodide having a specific gravity of 3.3. After separation the grains were washed with acetone. This gave products of over 99.5 per cent purity in all but a few cases where there was garnet present, which had a specific gravity above that of the hypersthene, or augite and/or hornblende, which had specific gravities below that of the hypersthene but above 3.3. In those cases, a rough specific gravity of the material was determined and two separations were made using Clerici solution. The first, with liquids of specific gravity just above that of the hypersthenes, in which case the impurities were separated as the heavy fractions. The second, with liquids having a specific gravity just below that of the hypersthenes, in which case the impurities were found in the light fractions. After separation, the grains were washed well with hot water to remove the thallous salts and dried at 110° C. In all samples, product purity was above 99.5 per cent.

At all stages during the purification process materials were examined with a binocular microscope. This allowed the examination of a large number of grains at one time. Impurities were seen quite easily because of the definite difference in color, luster and general appearance. The final product was also examined petrographically by making a balsam mount of a random sample.

PRINCIPLES OF THE CHEMICAL ANALYSIS

While none of the individual determinations are original, the method used is a combination of known methods best adapted for use with hypersthenes and related minerals. Some original innovations have been added. The analysis was carried out on a solution containing known amounts of the elements analyzed for, in the proportion in which they might be encountered. In all cases, satisfactory results were obtained.

One of the major changes in the analysis is the decomposition of the sample with hydrofluoric and perchloric acids, thereby introducing no extraneous sodium salts. At the same time, separate aliquots can be taken of optimum size for each determination. Silica is determined on a small separate sample by dehydration with perchloric acid and the resulting filtrate discarded because of the high concentration of sodium salts introduced by fusion. No attempt is made to separate calcium from the magnesium when analyzing for the latter, because of the high magnesium and low calcium content. Aluminum is determined directly because of its low percentage, and corrected only for titanium, present in even smaller amounts. The alkalies are determined after a hydrofluoric and perchloric acid decomposition. Before analyzing for chromium colorimetrically, hydrochloric acid is used instead of alcohol to remove manganate interference. Water is determined by volatilization and absorption. The other elements are determined in the usual way.

Procedure for the Chemical Analysis

1. *Specific Gravity.* This determination is made first so that the mineral can be recovered and used for subsequent analyses. Dry and weigh a 25 ml. pycnometer containing a thermometer, using a similar bottle as a tare. Fill the pycnometer with water and reweigh, noting the temperature of the water. From this weight and from the density of water at this temperature calculate the volume of the pycnometer. Check this result by weighing the pycnometer filled with water at different temperatures. This gives the weight of water contained in the pycnometer at any temperature.

Weigh 5 grams of the sample into the pycnometer by means of a powder funnel. Cover with about a quarter of an inch of water containing a wetting agent. Place the pycnometer in a desiccator and evacuate carefully with water suction so that none of the sample is lost by violent bubbling. Leave the pycnometer in the desiccator for 15 minutes, then remove, fill with water and allow to come to equilibrium in the balance case. Insert the thermometer, dry the pycnometer with a clean cloth, weigh quickly and note the temperature.

The amount of wetting agent added to the water is about 0.01 per cent, which has no appreciable effect on the density of the water. It aids the determination by preventing the entrapment of air by the sample. Fairly large fragments (about 100 mesh) are preferred for this determination. After use, the sample is washed well, dried and used for the chemical analysis.

2. *Water.* Weigh a 0.5 gram sample into a porcelain boat, place in a combustion tube and heat for 30 minutes at 1000° C., while passing dry air through the tube. Dry the air by passing it through anhydrous calcium chloride and anhydrous magnesium perchlorate. Collect the water in a weighed absorption bulb containing anhydrous magnesium perchlorate. Remove the bulb, place in the balance and reweigh after it reaches equilibrium. Run a blank determination under the same conditions of time and temperature.

3. *Silica.* The method is essentially the same as that of Willard and Cake (12). Fuse a 0.20 to 0.25 gram sample with sodium carbonate in a platinum crucible for 30 minutes. Leach the melt with dilute hydrochloric acid, add perchloric acid and evaporate to fumes. Continue fuming for 30 minutes, cool, dilute with water, filter and wash alternately with hot dilute hydrochloric acid and water until the paper is free of perchloric acid. Evaporate the filtrate to fumes and repeat the process. Combine the filter papers and ignite in a weighed platinum crucible. Cool and reweigh the crucible. Treat the residue in the crucible with a few drops of sulfuric acid and about 10 ml. of hydrofluoric acid, evaporate to dryness, ignite for 15 minutes, cool and reweigh. The loss in weight is equal to the weight of silica in the sample.

4. *Ferrous Iron.* The method of Soule (13) is used for this determination. Weigh a 0.5 gram sample into a round-bottomed flask containing a rubber stopper with an inlet and outlet tubes. Displace the air with a stream of carbon dioxide. Add 5 ml. of 1:1 sulfuric acid, 10 ml. of water and 15 ml. of hydrofluoric acid. Boil the solution gently with a continuous stream of carbon dioxide bubbling through the solution. Continue boiling until the mineral is dissolved completely. Allow to cool for 5 minutes under a stream of carbon dioxide. Add 100 ml. of a saturated solution of boric acid containing 2.5 per cent sulfuric acid. Cool the flask below room temperature and titrate with 0.1 N potassium permanganate solution.

5. *Sodium and Potassium.* The alkali metals are determined according to the method of Marvin and Woolaver (14). Weigh a 0.5 gram sample into a platinum dish and treat with 5 ml. of nitric acid, 10 ml. of perchloric acid and 10 ml. of hydrofluoric acid. Evaporate the solution to half of the volume and add 10 ml. of hydrofluoric acid. Evaporate to fumes of perchloric acid and continue heating for 15 minutes. Cool the solution, transfer with water to a pyrex beaker and evaporate to dryness. Bake the residue on a hot plate until no more fumes of perchloric acid are noted. Heat the sides of the beaker with a bunsen burner to remove the last traces of perchloric acid.

Cool, add 50 ml. of 10 per cent ammonium hydroxide and boil for 10 minutes. Filter and wash with 10 per cent ammonium hydroxide. Heat the filtrate to just below boiling and add 10 ml. of 5 per cent ammonium oxalate. Allow to stand one hour, filter and wash with water. Reheat the filtrate to 60° C. and add 5 drops of a 2 per cent solution of 8-hydroxyquinoline in 1:10 acetic acid. Allow to stand for one hour, filter and wash with water. Acidify the filtrate with hydrochloric acid and evaporate to dryness on the steam bath.

Treat the residue with aqua regia and evaporate to dryness with hydrochloric acid to insure the presence of only chlorides. Dissolve the residue in water and filter into a weighed platinum dish. Evaporate the filtrate to dryness on the steam bath, place in a cold muffle furnace and bring the temperature up to 550° C. slowly. Hold the furnace at that temperature for 30 minutes, remove the dish, cool and weigh. The increase in weight is mixed sodium and potassium chlorides.

The amount of sodium present in the mixed chlorides is determined by the method of Kolthoff and Sandell (15). Dissolve the chlorides in water and transfer to a beaker. Evaporate to dryness on the steam bath, add one ml. of water and 10 ml. of zinc uranyl acetate solution and stir well. Allow to stand one hour and then filter on a weighed porcelain crucible. Wash with small portions of the precipitating agent, five 2 ml. portions of ethyl alcohol saturated with the precipitate and finally with a small amount of acetone. Place the crucible in the balance case for 15 minutes and reweigh. The increase in weight is sodium zinc uranyl acetate with six molecules of water of crystallization and is calculated to an equivalent weight of sodium chloride which is subtracted from the weight of the mixed chlorides. The per cent of sodium and potassium oxides is then calculated. A blank determination is made using the same reagents.

6. *Chromium.* Mix a 0.1 gram sample with 3 grams of sodium carbonate in a platinum crucible and fuse for 30 minutes. Cool and leach with hot water. Filter the residue and wash with hot water containing a little sodium carbonate. Add 6 ml. of 1:1 sulfuric acid which will give the correct acidity (0.2N) on final dilution. Add 5 drops of concentrated hydrochloric acid and heat on the steam bath for an hour to reduce any manganate which is present. Cool and transfer to a 100 ml. volumetric flask. Add 2 ml. of a 0.25 per cent alcoholic diphenylcarbazide solution and dilute to the mark with water. Compare the intensity of the color obtained with a standard solution of potassium dichromate treated in the same way, using a colorimeter with a green filter.

7. *Decomposition of the Sample for the Determination of Aluminum, Ferric Iron, Titanium Manganese, Calcium, Magnesium and Nickel.*

Weigh a 2 gram sample into a platinum dish and add 10 ml. of perchloric acid, 5 ml. of nitric acid and 10 ml. of hydrofluoric acid. Heat the dish on the hot plate until the solution has decreased to half the volume, add 10 ml. of hydrofluoric acid and then evaporate almost to dryness. Cool, take up with water and transfer to a beaker. To assure recovery of all the salts, add 5 ml. of 1:1 hydrochloric acid to the dish, heat and transfer to the same beaker. Repeat this treatment 3 times or until all the salts are transferred to the beaker. Dilute to about 200 ml. and boil until all the salts are dissolved. Cool, add 20 ml. of hydrochloric acid, transfer with water to a 500 ml. volumetric flask and dilute to the mark.

8. *Ferric Iron.* Pipet a 200 ml. aliquot into a beaker and evaporate to 25 ml. Add 15 per cent stannous chloride dropwise to the hot solution until the yellow color of ferric chloride disappears and then add 2 drops in excess. Cool and add rapidly to the solution 10 ml. of a saturated mercuric chloride solution. Dilute to about 250 ml., add 10 ml. of phosphoric acid and titrate with 0.1 N potassium dichromate using diphenylamine sulfonic acid as indicator.

The total amount of iron present is calculated as ferric oxide. From this is subtracted the amount of iron known to be present in the ferrous state. This gives the amount of ferric oxide actually present in the sample.

9. *Aluminum and Titanium.* The method used for the determination of these elements is that given by Willard and Diehl (16). Pipet a 100 ml. aliquot from the original solution into a beaker, dilute to 400 ml. and add 3 grams of diammonium hydrogen phosphate. Neutralize most of the free acid with ammonium hydroxide and then add just enough to give a faint permanent precipitate. Add 2 ml. of concentrated hydrochloric acid and stir the solution until it becomes clear. Add 20 ml. of water containing 15 grams of sodium thiosulfate and heat to boiling. Add 8 ml. of glacial acetic acid and 5 grams of ammonium acetate and boil vigorously for 30 minutes. Filter while the solution is still hot and wash with water.

Transfer the filter paper to the original beaker and add 10 ml. of hydrochloric acid and 50 ml. of water. Boil for a few minutes to dissolve the precipitate, filter and wash with 1:10 hydrochloric acid. Dilute the filtrate to 300 ml. and precipitate as before. Filter and wash this precipitate with water. Place the filter paper containing the precipitate in a weighed porcelain crucible, ignite and reweigh the crucible. The increase in weight is due to combined aluminum and titanium phosphates.

Add 3 to 4 grams of potassium pyrosulfate to the residue and fuse until it has dissolved completely. Cool and leach with 50 ml. of 1:1 sulfuric acid. Transfer with water to a 100 ml. volumetric flask, add 5 ml. of hydrogen peroxide (3 per cent) and dilute to the mark. Compare the intensity of the color formed with that of a standard titanium solution treated in the same way, using a colorimeter with a blue filter.

The amount of titanium oxide present in the sample is calculated, converted to titanium phosphate and subtracted from the weight of combined phosphates above. The remainder is aluminum phosphate, which is calculated to aluminum oxide.

10. *Calcium.* The method used for calcium is a modification of that given by Caley and Elving (17). Pipet a 100 ml. aliquot into a beaker, add 10 ml. of perchloric acid and 5 ml. of nitric acid and evaporate to dryness. Bake the residue on the hot plate and heat the beaker with the direct flame of a Bunsen burner to assure the removal of all the perchloric acid. Cool, add 200 ml. of water and boil for 15 minutes. Filter through a fine filter paper and evaporate the filtrate to dryness. Add 9 ml. of water, 10 drops of 1:1 sulfuric acid and 100 ml. of methyl alcohol. Allow to stand overnight and filter through a weighed fine porcelain filtering crucible. Wash with 90 per cent methyl alcohol, dry the precipitate for 30 minutes at 100° and ignite for 30 minutes above 450° C. Cool and weigh as calcium sulfate.

11. *Magnesium.* Pipet a 25 ml. aliquot into a beaker and dilute to 200 ml. Add 2 grams of ammonium chloride, heat the solution almost to boiling and add ammonium hydroxide until it is just alkaline to litmus. Add 5 ml. of saturated bromine water, test the solution to make sure it is still ammoniacal and then boil for 15 minutes. Filter the precipitate while the solution is still hot, wash well with water, dissolve it off the paper with hot dilute hydrochloric acid and reprecipitate as above. Combine the two filtrates, make just acid with hydrochloric acid and add 0.5 gram of diammonium hydrogen phosphate. Cool below room temperature, add ammonium hydroxide dropwise until the solution is just basic, allow the

calcium and magnesium to precipitate and then add an excess of 30 ml. of ammonium hydroxide. Stir the solution occasionally during the next 30 minutes and allow to stand overnight. Filter the precipitate through paper, wash with 1:20 ammonium hydroxide, dissolve off the paper with 1:10 hydrochloric acid and reprecipitate as above. Filter this precipitate through a weighed porcelain filtering crucible, wash with 1:20 ammonium hydroxide, dry and ignite for one hour. Cool and reweigh as combined magnesium pyrophosphate and calcium orthophosphate. The amount of calcium phosphate known to be present is subtracted and the percentage of magnesium oxide calculated.

12. *Manganese.* The method recommended by Willard and Greathouse (18) is used for the determination of manganese. Pipet a 25 ml. aliquot into a beaker, add 10 ml. of nitric acid and evaporate almost to dryness to expel the hydrochloric acid. Repeat until all the hydrochloric acid is removed. Add 10 ml. of nitric acid, 25 ml. of water and 5 ml. of phosphoric acid and heat the solution to boiling. Add 0.5 gram of potassium periodate, boil until the color of permanganate appears and continue boiling for a few minutes. Cool and dilute to the mark with water in a 100 ml. volumetric flask. Compare the intensity of the color with that of a standard manganese solution treated in the same way, using a colorimeter with a green filter.

13. *Nickel.* The method used is that given by Sandell (19). Pipet a 25 ml. aliquot into a 100 ml. volumetric flask and add 5 ml. of 10 per cent citric acid and 2 ml. of saturated bromine water. Neutralize the solution with ammonium hydroxide and add 3 or 4 drops in excess. Add 1 ml. of a 1 per cent alcoholic dimethylglyoxime solution and dilute to the mark with water. Compare the intensity of the color formed with that of a standard nickel solution treated in the same way and containing an equivalent amount of iron as known to be present in the sample. The comparison is made by means of a colorimeter using a green filter.

Determination of Optical Properties

1. *Volume Analysis of the Rock*

The volume analysis of the rock was made on a thin section using a Wentworth integrating stage. Five traverses were made perpendicular to any foliation, if present, and these results were averaged.

2. *Anorthite Content of the Plagioclase*

The anorthite content of the plagioclase in the rock was determined by measuring the indices of refraction on cleavage flakes by the immersion method and applying the Tsuboi curves (20).

3. *Optic Angle of the Hypersthene*

The optic angle of the hypersthene was determined on the universal stage in white light. The measurements were made on a balsam mount of the purified grains and on a thin section of the original rock. The average of 10 to 15 determinations was taken. A correction was applied for the difference between the beta index of the mineral and the index of refraction of the hemisphere used, which was 1.649.

4. *Indices of Refraction of the Hypersthene*

The indices of refraction of the hypersthene were determined by the immersion method in sodium light. At least ten grains were checked for each index. The gamma index was measured on grains showing a centered acute bisectrix figure. The beta index was measured on both a centered acute bisectrix figure and an optic eye figure. The alpha index was measured on a centered obtuse bisectrix figure and a flash figure. Orientation of the grains was helped by the marked pleochroism of the hypersthenes.

The liquids used were measured on a Pulfrich refractometer, with corrections made for temperature differences. The liquids differed by 0.0020 to 0.0028 so that the indices of refraction of the minerals could be estimated to 0.001.

X-RAY AND SPECTROGRAPHIC DATA

The *x*-ray photographs were taken on finely ground powders using both chromium and copper targets. The photographs obtained were then measured and compared to data in the literature.

For the spectrographic determination, an ARL-Dietert 1.5 meter grating instrument was used. The samples were burned in an A.C. arc and the lines obtained compared to standard lines. No attempt at quantitative measurement was made.

DISCUSSION OF RESULTS

The analyses of the hypersthenes are listed in Table 1. All chemical analyses are averages of duplicate determinations with the greatest error of the duplicates being 0.5 per cent from the mean.

The limits of error in the specific gravity determinations are plus or minus 0.005. The optic angle determinations are correct to within 2 degrees and the index of refraction determinations to within 0.001.

The molecular percentage of ferrous metasilicate in each hypersthene was calculated by adding the number of moles of manganese and ferrous iron and dividing them by the total number of moles of magnesium, manganese and ferrous iron. No other elements were included. This method of calculating the percentage of ferrous silicate was decided upon as being the best and follows the method used by Henry (9) and by Hess and Phillips (4).

There are a few facts of interest which are not included in the tables. The strength of the pleochroism of the hypersthenes does not have any relation to the chemical composition. The pleochroism is red in the X direction, yellow-brown in the Y direction and green in the Z direction.

TABLE 1. ANALYTICAL DATA

	35–5	35–6	35–8	35–9
SiO_2	50.70	50.60	51.43	52.00
Al_2O_3	0.05	0.04	0.06	0.57
Fe_2O_3	1.18	1.44	1.39	1.34
FeO	25.65	26.02	23.60	22.46
MgO	20.29	19.49	20.69	21.62
CaO	0.66	0.87	1.02	0.75
Na_2O	0.06	0.07	0.46	0.46
K_2O	0.05	0.06	0.06	0.07
H_2O	0.22	0.28	0.32	0.28
TiO_2	0.17	0.17	0.18	0.14
Cr_2O_3	0.00	0.004	0.00	0.003
NiO	0.00	0.00	0.00	0.00
MnO	0.75	0.95	0.73	0.57
Total	99.78	99.99	99.94	100.26
% $FeSiO_3$	42.2	43.7	39.8	37.5
Sp. Gr.	3.557	3.560	3.512	3.510
2V	−52	−51	−55	−57
alpha	1.702	1.703	1.699	1.695
beta	1.711	1.713	1.708	1.705
gamma	1.716	1.718	1.713	1.710

	35–13	35–14	35–19	35–32
SiO_2	51.18	50.60	52.80	52.60
Al_2O_3	0.15	0.16	0.00	0.12
Fe_2O_3	1.85	0.97	1.67	0.95
FeO	25.16	25.71	18.65	17.14
MgO	18.00	18.96	24.95	25.65
CaO	1.87	1.65	1.05	2.17
Na_2O	0.42	0.07	0.44	0.88
K_2O	0.25	0.60	0.01	0.00
H_2O	0.28	0.44	0.14	0.14
TiO_2	0.25	0.19	0.09	0.15
Cr_2O_3	0.02	0.10	0.02	0.06
NiO	0.00	0.00	0.01	0.05
MnO	0.38	0.31	0.43	0.41
Total	99.81	99.76	100.26	100.32
% $FeSiO_3$	44.3	43.5	30.0	27.8
Sp. Gr.	3.536	3.530	3.463	3.431
2V	−51	−53	−64	−69
alpha	1.703	1.703	1.685	1.685
beta	1.713	1.713	1.695	1.695
gamma	1.717	1.717	1.700	1.700

The most strongly pleochroic of all the hypersthenes is sample 35-9, which has a lower ferrous silicate content than most of the others. Both samples 35-14 and 35-19 show weak pleochroism. This is surprising since sample 35-14 has the highest ferrous silicate content of all the samples. All the others show medium pleochroism.

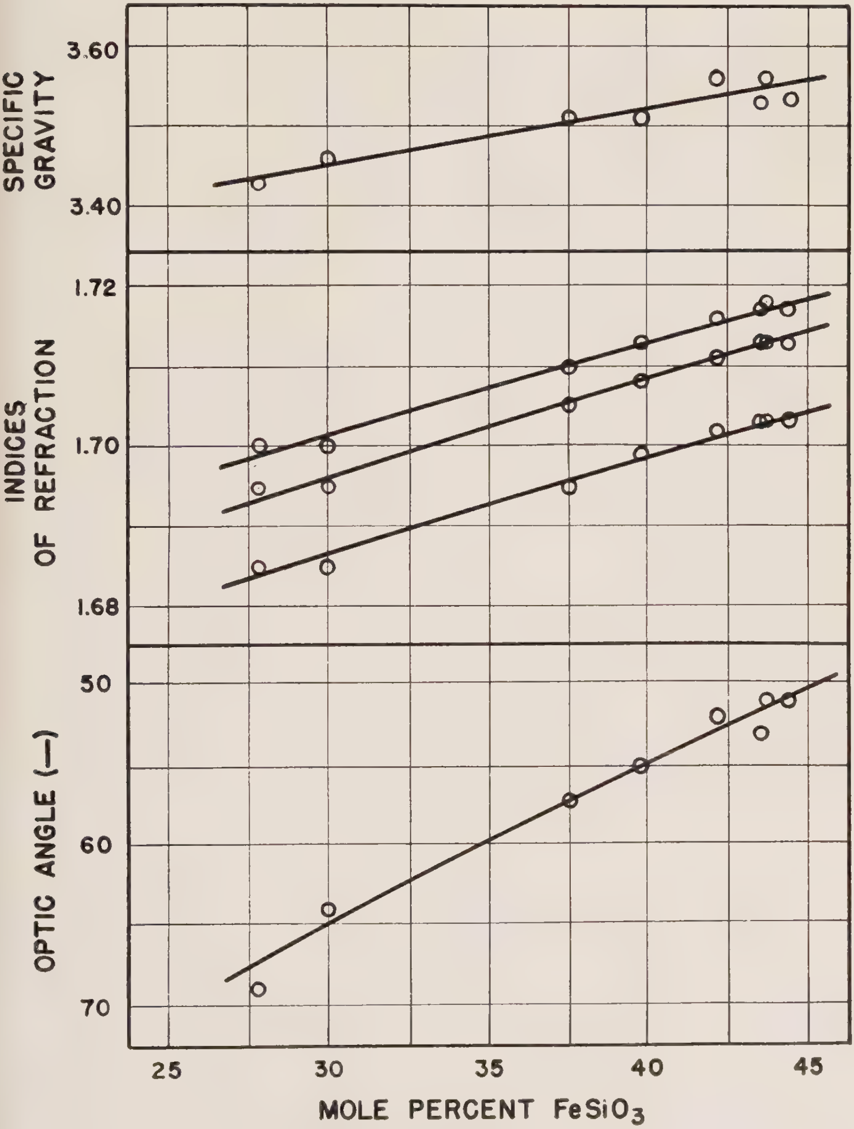

FIG. 1. Curves for optical properties and specific gravity of hypersthenes.

The colors of the minerals by reflected light are as expected. That is, those with high iron content are dark brown and those with low iron content are light brown. There is one exception and that is sample 35-32. It has the lowest iron content of all but its color is darker than any except samples 35-13 and 35-14, which have a very high iron content.

The variation of the optic angle, indices of refraction and specific gravity with chemical composition of the hypersthenes is plotted on Fig. 1. Within the limits of error, the points fall very well on the curves.

The curves do not agree exactly with any previous ones published for this series. However, the shapes of the curves are similar and it may be that the only difference is one of chemical composition. If the curves drawn by Hess and Phillips (4) were moved by an increase of three mole per cent ferrous silicate, they would correspond to the ones presented here. If those of Henry (9) were moved by a decrease of 6 mole per cent ferrous silicate, they would correspond. Except for the optic angle curve, those of Poldervaart (10) would correspond if moved by an increase of 3 per cent. So it seems that the controversy is concerned with the chemical analyses. It is felt that the previous analytical methods may have been in error enough to cause the curves to differ as they do.

The curves published in Winchell's latest text (11) are hard to interpret. They do not show the regularity in respect to the present curves, as do the other curves. The optic angle curve would have to be moved by a decrease of 9 mole per cent, the index of refraction curve by an increase of one mole per cent, and the specific gravity curve by a decrease of 4 mole per cent. However, since there is no reference as to the source of these curves, no further comment can be made.

In Table 2 are listed the interplanar distances (in Angstrom units) of the strongest reflections as obtained with these hypersthenes and those listed in the American Society for Testing Materials card index, 1945 supplement, for hypersthene, II-1133, and for enstatite, II-1186.

TABLE 2. X-RAY DATA

Hypersthene Collection 35	*Hypersthene* II-1133	*Enstatite* II-1186
3.14 (10)	3.20 (10)	3.16 (10)
1.47 (8)	1.49 (8)	1.48 (6)
2.86 (6)	2.89 (8)	2.85 (6)
2.49 (6)	2.48 (5)	2.53 (6)
2.07 (6)	2.11 (5)	2.11 (6)
1.59 (3)	1.60 (6)	1.60 (5)
1.38 (3)	1.39 (6)	1.39 (5)
1.29 (3)	1.30 (5)	1.29 (3)

In parentheses are the relative intensities of the reflections. It can be seen that the values obtained for these samples check very well with the accepted ones for hypersthene and enstatite.

Within the limits of error of measurement of the lines, there is no difference in the spacing between the hypersthene with the lowest iron content and that with the highest. There was a distinct decrease in the intensity of the reflections from the minerals with the most iron. This was not due to a change in the intensity of the reflections but to an increase in absorption of the *x*-ray by the iron content of the samples. With such a high iron content, practically all of the radiation from both the copper and chromium targets was absorbed.

Table 3 lists the results of the spectrographic analysis.

TABLE 3. SPECTROGRAPHIC DATA

(Elements not chemically analyzed)

+ element present
− element absent

Sample 35-	5	6	8	9	13	14	19	32
Cu	+	−	+	+	+	+	+	+
Co	+	−	+	+	+	+	+	+
V	+	+	+	+	+	+	+	+
Li	−	−	−	−	−	−	−	−
Zn	−	−	−	−	−	−	−	−
Pb	−	−	−	−	+	+	−	−
Ag	−	−	−	−	−	+	−	+
Sn	−	−	−	−	−	−	−	−
Mo	−	−	−	−	−	−	−	−
U	−	−	−	−	−	−	−	−

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SOME HORNBLENDES FROM SOUTHEASTERN PENNSYLVANIA AND DELAWARE[1]

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ABSTRACT

A group of eight hornblendes from the Piedmont region of Pennsylvania and Delaware were studied with special reference to their genetic relationships. Chemical analyses and optical data are presented. The relationship of optical properties and composition are discussed generally. Substitution of heavy metals for magnesium has the greatest influence on optical properties. Both refractive index and optic angle (+2V) increase with increasing heavy metal substitution. Substitution of aluminum for silicon has a similar effect on refractive index, but decreases the optic angle.

Potash and soda content of the hornblendes is correlated with degree of granitization of the host rock. Both total potash and the K/Na ratio in the vacant positions of the lattice increase with greater alteration.

INTRODUCTION

The piedmont province in Pennsylvania and Delaware has been studied for many years from a structural and petrologic standpoint. Excellent detailed studies of the petrography and structure of the metamorphic rocks in the area are available, but the mineralogy of the more complex constituents of these rocks has been neglected. A more thorough knowledge of the chemical characteristics of such common, but complex, silicates as the pyroxenes, amphiboles, micas, and garnets which occur in these rocks would be of great value in the interpretation of petologic phenomena. This paper, together with the recent work of Clavan, Mcnabb and Watson (1954) on the ortho-pyroxenes of this region, is meant as the beginning of such a study of these minerals.

The regional geology has been described in several folios covering the area (Bascom et al. 1909, 1920, 1932). The major rock types in the area are metagabbros, migmatites, and granite gneisses of pre-Cambrian age, metamorphosed sediments (schists, phyllites and limestones) of pre-Cambrian or early Paleozoic age, and Triassic sediments of the Newark series. The age and structure of many of these rocks is still a matter of controversy and these questions are not discussed here.

This paper deals with the mineralogy and petrologic relationships of some hornblendes from the metamorphic rocks in the area.

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Occurrence of the Hornblendes Studied

The samples taken for separation of hornblendes for analysis represent several different but characteristic rock types of the Piedmont region. Individual samples were selected in such a way as to be representative of the rock type and at the same time have the least variation. In order to obtain valid correlations between rock type, hornblende composition, and hornblende properties the samples were taken from a single outcrop chosen for the uniformity of its material. The locations of the samples are listed below, including a grid index on the 15 minute quadrangle maps for the area.

35-2—Chester 14373—500 feet northeast of Upper Bridge, Crum Creek Reservoir. A course-grained pegmatoid schlieren in Baltimore gneiss. In the immediate area there are numerous gabbroic xenoliths in varying stages of alteration or assimilation by felsic material.

35-5—West Chester 92755—0.1 mile north of crossroads at Tallyville, Delaware (U. S. Route 202). A medium fine-grained eucritic norite showing a slight gneissic banding; a portion of the variable metagabbro mass known as the Wilmington gabbro.

35-10—Wilmington 17328—White Clay Creek west of bridge on Delaware Route 2. A hornblende gneiss alternating with bands of granite gneiss. Small stock-like intrusions of microcline rich pegmatites cross-cut both rock types. These rocks are grouped witn the Port Deposit granodiorite which is intrusive into the Wilmington gabbro.

35-11—Elkton 63651—300 feet west of bridge over Christiana Creek. A very coarse-grained portion of the Wilmington gabbro which becomes still coarser to the northeast, and finer-grained and more massive on Chestnut Hill and Iron Hill to the southwest.

35-22—Norristown 89781—Small quarry on knoll 0.5 mile southwest of Ithan Creek and Bryn Mawr Avenue. A hornblende gneiss member of the Wissahickon formation. These hornblende gneisses have been described in detail by Weiss (1949).

35-27—Chester 29959—Center of Springfield Granite Quarry. A 1 to 3 foot wide band of hornblende-biotite schist in the Springfield granodiorite. This rock type has been shown by Postel to be a granitized equivalent of the hornblende gneiss members of the Wissahickon schist.

35-29—Burlington 18779—Van Artsdalen's Quarry. A massive medium-grained gabbro in the form of "boudins," from broken and deformed dikes enclosed in coarse marble which is surrounded by a dioritic gabbro. Some of the metagabbros within the quarry are rich in scapolite. A detailed discussion of the petrology of this area is given by Weiss (1947).

35-31—Wilmington 22458—Cut on the Landenburg Branch of the Baltimore and Ohio Railroad, 0.5 mile northeast of Marshaltown, Delaware. A medium-grained, massive metagabbro belonging to the Wilmington gabbro mass. Locally the quartz content becomes very high, and occasional narrow veins of quarts cross cut the rock.

A volume per cent analysis made on thin sections of the samples described above is given in Table 1.

Separation of the Hornblendes

Crushing and Optimum Grain Size

The crushing of the relatively large quantities of material needed was readily accomplished by use of a small jaw crusher, a roller mill, and a

TABLE 1

Sample	35-2	35-5	35-10	35-11	35-22	35-27	35-29	35-31
hornblende	28	21	58	56	59	38	67	36
augite	—	8	—	—	—	—	11	5
hypersthene	—	10	—	—	—	—	—	—
plagioclase								
comp.	An_{30}	An_{72}	An_{34}	An_{66}	An_{37}	An_{34}	An_{51}	An_{57}
albite	18	16	20	14	9	20	10	15
anorthite	8	41	11	28	5	10	11	26
potash feld.	2	—	—	—	—	—	—	—
quartz	24	—	5	—	20	6	—	8
biotite	16	—	3	—	—	20	—	—
magnetite	4	4	—	1	7	—	3	10
clinozoisite	—	—	3	1	—	3	—	—
sphene	—	—	—	—	—	3	—	—

ball mill, in that order. The crushed material was sieved, and the 100 to 150 mesh fraction was taken for separation.

In almost all cases material coarser than 100 mesh contained too many combined grains, that is, grains composed of more than one mineral. As the grain size is decreased from 150 mesh, separation operations become more difficult. The fraction between 100 and 150 mesh has the least number of combined grains, is easy to handle in separation, and can be used directly for chemical analysis and optical study.

Separation Methods

Prior to the separation itself it was found necessary to remove all dust or finely ground material from the sample. This was accomplished by wet screening the sample on a 200 mesh screen and drying after the removal of the excess water by acetone. Dust free grains give better separations by magnetic methods, and are easier to wash in heavy liquid separations. Removal of water prior to drying lessens the danger of oxidation of ferrous iron present in the sample.

A good separation of hornblende from most of the constituents of the rocks in question can be easily and rapidly made by use of the Franz isodynamic separator (Franz in Gaudin and Spedden, 1943). The following procedure was used:

(*a*) The feeder trough of the separator was set at an angle of 25° parallel to it and 15° at right angles to it. This trough orientation was found satisfactory for all steps.

(*b*) Highly magnetic material such as magnetite, ilmenite, and pyrrhotite was first removed by a hand magnet.

(*c*) The material was then passed through the separator at a very low intensity field (0.1 ampere). This removed such minerals as hematite, limonite, pyrite, and magnetite present as inclusions in the grains. The non-magnetic fraction was passed through once or twice more: being the fraction of greater volume it sweeps some of the magnetic material along with it and several passes are necessary for a complete separation. This procedure of repeated separations at the same field intensity was followed in all subsequent steps.

(*d*) The non-magnetic portion from (*c*) was run through at a high field intensity (1.0 ampere). This separates most of the mafic minerals from quartz and feldspar.

(*e*) Several passes were made on the magnetic fraction from (*d*) at intensities gradually increasing from that in (*c*). These steps removed minerals more magnetic than hornblende such as hypersthene and garnet.

(*f*) Several passes were then made on the non-magnetic fraction from (*e*) at intensities gradually decreasing from (*d*). These steps removed minerals less magnetic than hornblende, such as muscovite, diopside, and most augites.

This general procedure often resulted in the concentration of hornblende to 90 per cent or better. In some cases, however, large amounts of iron rich biotite and augite were present, and the hornblendes could not be separated from them by the isodynamic separator.

Further separation and purification of the samples was accomplished by heavy liquid techniques. By initial use of magnetic separation the volume of sample was reduced sufficiently for these methods to be practicable. Felsic minerals were removed by bromoform. Augite and biotite were removed by methylene iodide whose specific gravity was adjusted to points just above and below that of the hornblende by the addition of small amounts of acetone.

The sample taken for analysis was examined for purity and, where necessary, some hand picking was done. All samples analyzed contained no more than traces of foreign minerals.

Non Uniformity of Mineral Grains

Several of the hornblendes encountered were found to have a rather large range in specific gravity. Optical examination of these samples especially in thin section showed a marked color zoning of individual grains. It was assumed that these samples were variable in composition, and they were discarded from this work.

CHEMICAL COMPOSITION OF THE HORNBLENDES

Discussion of Analytical Methods

The analytical procedure used was essentially that as outlined by Washington (1930) for the analysis of silicate rocks, with slight modifications for the specific problems at hand. Although the analyses are reported to the second decimal, this last place is not regarded as really significant. Errors inherent in the analytical methods as well as those introduced by the slight variation in composition of the mineral do not permit such precision.

In all of the analyses, material of 100–150 mesh was used except in the alkali determinations where the sample was ground to −325 mesh. Alkalies were determined by the J. Lawrence Smith method. Total iron was determined on the total R_2O_3 group by reduction with hydrogen sulfide and titration with permanganate. Ferric iron and aluminum were determined by difference. Water was determined by the Penfield method. Some of the specific analytical procedures are given in greater detail below:

Ferrous Iron—The problem of oxidation of ferrous iron during grinding was almost completely eliminated by the use of coarse-grained (100–150 mesh) samples. The decomposition was effected readily and rapidly by use of a sulfuric-hydrofluoric acid mixture in a covered platinum crucible. Titration of the resulting solution with permanganate gave reproducible results.

Fluorine—The fluorine determination was carried out according to the method of Willard and Winter (1933), with slight modification adapting it to the analysis of glass.* In brief the method is as follows: A mixture of 1 part sample, 1.5 parts ZnO and 10 parts Na_2CO_3 is fused in a platinum dish. The fusion is disintegrated and digested with hot water, and filtered into the distillation flask.† The flask is connected to the still head and 15 cc.of concentrated sulfuric acid are added dropwise. The solution is boiled until a temperature of 135° C. is reached, and the distillate is collected. The solution is maintained at this temperature until an additional 100 cc. of distillate is obtained. The distillate is made alkaline to phenolpthalein, by the addition of dilute NaOH, and is evaporated to a volume of 25 cc. The solution is cooled and 25 cc. of 95% ethyl alcohol are added. Five drops of sodium alizarin sulfonate are added and the solution acidified with dilute HCl. The fluosilicic acid now in solution is titrated with a standard thorium nitrate solution to the formation of a pink lake with the indicator reagent.

Silica—The presence of appreciable amounts of fluorine in silicates causes a low value for silica, due to the loss of a small amount as the tetrafluoride during the fusion. In most cases the amount of fluorine present was small enough so that the addition of a small amount of borax to the carbonate fusion was sufficient to remove almost all of the fluorine and prevent its interference (Hillebrand & Lundell, p. 537).

Water—Hygroscopic water was not determined. Since the samples were subjected to repeated washings with both water and acetone prior to the analysis, it is believed that a determination of this constituent would be meaningless.

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* Personal communication, H. S. Moser, Kimble Glass Co., Vineland, New Jersey.

† The apparatus, described by Willard and Winter, was made by the Scientific Glass Apparatus Co., Bloomfield, New Jersey.

DISCUSSION OF THE ANALYSES

The complete analyses of eight hornblendes of the southeastern Pennsylvania-Delaware area are given in Table 2. The significance of the differences is more fully discussed in the section on atomic constitution, but several marked differences and similarities in composition can be pointed out here.

TABLE 2

Sample	35-2	35-5	35-10	35-11	35-22	35-27	35-29	35-31
SiO_2	42.90	44.94	45.09	48.71	42.65	45.28	43.33	44.73
Al_2O_3	11.92	11.24	10.43	9.48	15.89	11.00	15.28	11.54
TiO_2	1.44	1.79	0.84	0.32	0.65	1.01	1.23	1.32
Fe_2O_3	5.04	2.87	3.90	2.33	5.33	4.42	1.11	2.87
FeO	12.58	12.61	10.14	9.12	14.69	10.50	8.89	11.07
MgO	10.30	11.98	12.52	14.43	6.64	12.02	13.77	11.89
MnO	0.30	0.22	0.24	0.23	0.43	0.28	0.13	0.40
CaO	11.49	11.61	12.29	11.93	10.13	12.48	12.15	11.83
Na_2O	2.40	1.86	1.60	1.16	2.08	1.59	2.41	1.45
K_2O	1.19	0.47	0.78	0.15	0.28	0.97	0.87	0.60
H_2O	1.32	1.26	1.76	1.83	1.64	1.02	0.85	1.79
F	0.20	0.24	0.28	0.23	0.27	0.31	0.73	0.16
Cl	tr.	—	—	—	—	—	0.06	—
Total	101.08	101.09	99.87	99.92	100.68	100.82	100.81	99.65
O for F	0.08	0.10	0.12	0.10	0.11	0.13	0.32	0.07
Corr. total	101.00	100.99	99.75	99.82	100.57	100.69	100.49	99.58

Silica content is generally low, except in 35-11 where it is higher and associated with a lower alumina. Alumina is unusually high in 35-22 and 35-29. Sample 35-22 is unique in its very high iron content, low calcium and high sodium content.

Titania is interesting in that it varies by a factor of as much as five. Although the total amount of this metal is not great it is believed that it has a marked influence on the color of the hornblende.

Variations in the alkalies are also of special interest. High potash content generally corresponds to a relatively high soda content. The converse is not necessarily true. High soda may be more closely correlated with high alumina. Samples 35-2 and 35-27, showing the highest potash content, are from areas generally regarded as having been granitized.

Fluorine content is generally low and constant. Sample 35-29, associated with the scapolite metagabbro, has a higher fluorine and an appreciable chlorine content.

ATOMIC CONSTITUTION OF THE HORNBLENDES

The most useful and significant method of representing mineralogical compositions is in terms of mole per cent of each element present. This method is useful because it gives the true proportion between the various constituents. In the case of many silicate minerals the crystal structure has been determined, making it possible to determine the actual number of atoms of each element in a unit cell of the structure. Where several isomorphous substitutions are taking place simultaneously it is difficult to follow them when a mole per cent representation is being used, but an atoms per cell representation makes all the steps immediately apparent. The structure of tremolite has been determined by Warren (1929), and by the applications of Pauling's rules of isomorphous substitution he has discussed the nature of the structure of the more complex amphiboles such as hornblende. Since this structure has been almost universally accepted, it was assumed in the recalculation of the present analyses. In Table 3 the composition of the analyzed hornblendes is given in terms of

TABLE 3

Sample	35-2	35-5	35-10	35-11	35-22	35-27	35-29	35-31
Si	6.38	6.62	6.65	6.99	6.34	6.67	6.32	6.59
Al_s*	1.62	1.38	1.35	1.01	1.66	1.33	1.68	1.41
Al_y*	0.47	0.57	0.46	0.59	1.13	0.58	0.95	0.60
Ti	0.16	0.19	0.09	0.03	0.07	0.11	0.13	0.15
Fe'''	0.56	0.32	0.43	0.25	0.60	0.49	0.12	0.32
Fe''	1.56	1.55	1.25	1.09	1.82	1.29	1.09	1.36
Mg	2.28	2.63	2.74	3.09	1.46	2.62	3.00	2.61
Mn	0.04	0.03	0.03	0.03	0.05	0.04	0.02	0.05
Ca	1.83	1.83	1.94	1.84	1.62	1.97	1.90	1.87
Na	0.69	0.53	0.46	0.32	0.60	0.46	0.68	0.42
K	0.22	0.09	0.15	0.03	0.05	0.18	0.16	0.12
OH	1.30	1.24	1.73	1.76	1.63	1.01	0.83	1.76
F	0.10	0.12	0.13	0.10	0.13	0.14	0.33	0.07
Cl	—	—	—	—	—	—	0.02	—
Y group	5.07	5.29	5.00	5.08	5.13	5.13	5.29	5.09
$Mg+Al_y/Y$	0.54	0.61	0.64	0.72	0.51	0.62	0.75	0.63
Na+K in AA'	0.74	0.45	0.55	0.19	0.27	0.61	0.74	0.41
Fe'''/Fe''	0.36	0.21	0.34	0.23	0.33	0.38	0.11	0.24

* Sufficient aluminum was taken to make up the number of metal atoms in the chain to eight. This aluminum is designated as Al_s while the remainder is assumed to replace Mg and is designated as Al_y.

atoms per unit cell calculated on the basis of a total of 24 atoms of oxygen, fluorine, and hydroxyl groups. The general formula of the amphiboles as given by Larsen and Berman (1931) is as follows:

$$(Ca, Na)_2(Na, K)_{0-1}Mg(Mg, Al)_4(Al, Si)_2Si_6O_{22}(O, OH, F)_2.$$

In this work the group [$Mg(Mg, Al)_4$] will be refered to as the Y group. Within it the following additional substitutions may take place. Fe'' and Mn'' may replace the Mg, and Fe''' and Ti may replace the Al. If the values given in Table 3 are compared to this general formula, they will be seen to correspond quite closely.

Since many of the isomorphous substitutions are such that elements of different valencies may replace each other, it is obvious that they cannot be completely independent variables; a deficiency caused by one replacement must be made up in a second one. The replacement of silicon by aluminum in the chains tends to activate the oxygens of the chain and permit the introduction of alkalies in the so-called vacant positions AA' of the lattice (Warren, 1930). The effect of the Si-Al replacement may also be offset by the introduction of trivalent atoms in the Y group. A crude but definite proportionality between aluminum in the chain and total alkalies may be seen in the data given. The number of hydroxyl groups plus fluorine often falls below two, the difference supposedly being oxygen. This is to be expected if the content of trivalent atoms in the Y group rises to a high value, and indeed is typical of the oxyhornblende or basaltic hornblende in which the ferric iron content is very high. The Y group total occasionally increases to about five per cent over its correct value of 5. This is apparently not uncommon in hornblende analyses (Hallimond, 1943), but no attempt at explaining it seems to have been made. The smaller deviations from the total of five might be accounted for by the normal errors of the analysis, since the errors would be cumulative. The larger deviations, however, seem too large to be explained in this way. The only solution which seems to suggest itself is that a small amount of magnesium, in spite of its appreciably smaller ionic radius, may replace calcium.

Physical Properties of the Hornblendes

Specific Gravity

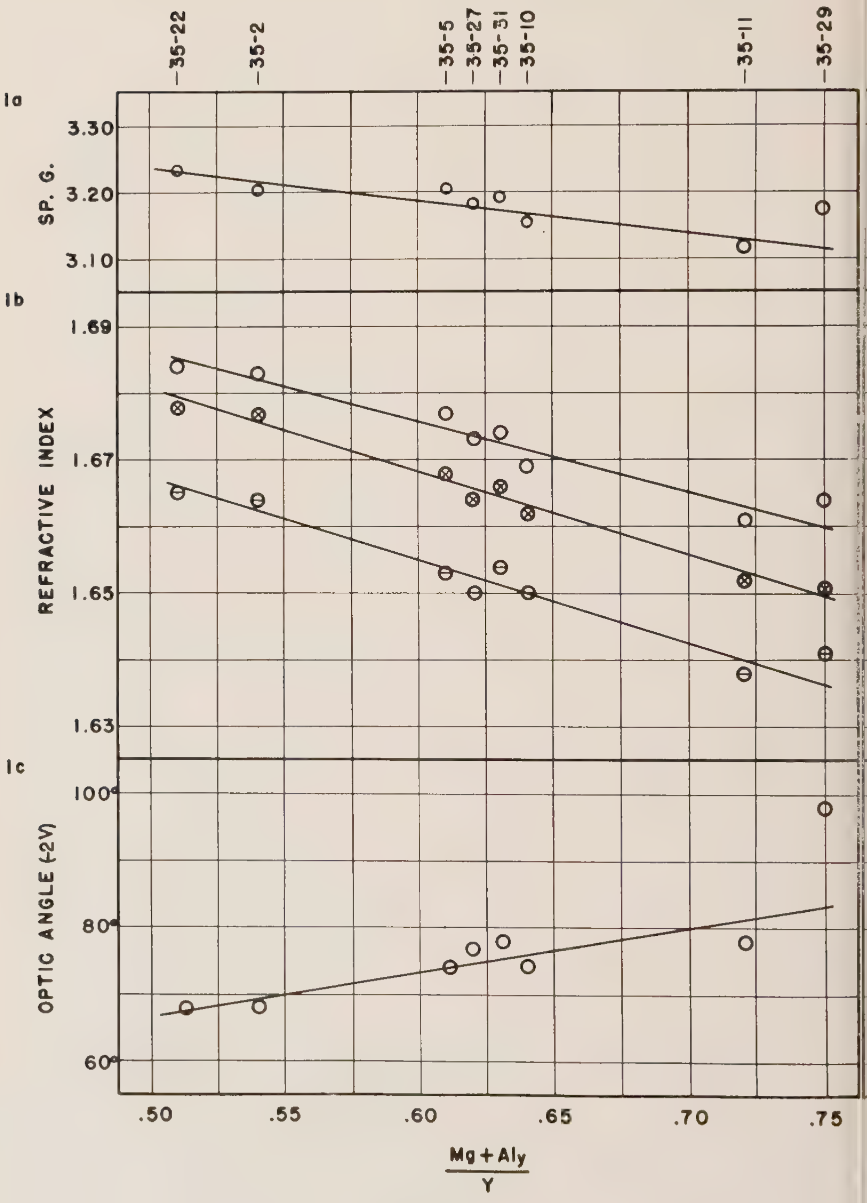
Specific gravities of the hornblendes were determined by the pycnometer method. Boiled, distilled water to which a trace of detergent was added as a wetting agent was the medium used. The density of this medium at 20° C. was 0.9986 g./cc. The specific gravities, as shown in Table 4, vary from 3.115 in the actinolitic member (35-11) to 3.234 in the iron and aluminum rich member (35-22). From the substitutions known to be possible in the amphibole molecule, it can be predicted that the greatest effect on specific gravity would be that due to the substitution of heavy ions such as Fe'', Fe''', and Ti'''' in the Y group in place of Mg''. Replacement of either Mg'' or Si'''' by Al''' would have little effect insofar as changing the molecular weight of the molecule. Substitution of aluminum in the chain, however, might have a considerable effect on the cell volume and would therefore influence the specific gravity. Data on cell dimensions of amphiboles is sparse (Warren, 1930), but an estimated change in unit cell volume of 0.5 per cent is probably not excessive. Such a change in unit cell volume would cause a change of about 0.01 in specific gravity. Figure 1*a* shows the relationship of specific gravity to increasing value of the $Mg+Al_y/Y$ ratio (equivalent to decreased heavy metals in the Y position). It will be noted that where points deviate from the line drawn, those lying above it generally have a large amount of aluminum in the chain. Where high aluminum is combined with low heavy metals (35-29) this deviation is greatest. The hornblende 35-29 is unique in all of its physical properties and, as will be seen later, should properly be called pargasite.

TABLE 4

Sample	Sp. G. ±0.002
35-2	3.203
35-5	3.204
35-10	3.153
35-11	3.115
35-22	3.234
35-27	3.181
35-29	3.175
35-31	3.192

OPTICAL PROPERTIES

Table 5 lists the optical properties of the eight analyzed hornblendes. Refractive indices were determined by the immersion method, using liquids whose indices were spaced about 0.0025 apart. The accuracy of index determinations is estimated as ±0.001. The optic angle and orientation were determined on a four circle universal stage. Since one optic axis generally fell outside the range of the stage, it was necessary to determine the optic angle by measuring V rather than 2V. This reduced the accuracy of these measurements to about ±3 degrees. The values of optic angles calculated from the refractive indices are in good agreement



35-22
35-2
35-5
35-27
35-31
35-10
35-11
35-29
Ia
SP. G.
3.30
3.20
3.10
Ib
REFRACTIVE INDEX
1.69
1.67
1.65
1.63
Ic
OPTIC ANGLE (-2V)
100°
80°
60°
.50
.55
.60
.65
.70
.75
Mg + Aly / Y

Fig. 1

with the measured values. All of the above measurements were made by sodium light. Pleochroic colors were observed on thin sections of standard thickness on the universal stage. An ordinary tungsten filament light source with a thin blue filter was used.

TABLE 5

Sample	35-2	35-5	35-10	35-11	35-22	35-27	35-29	35-31
α	1.664	1.653	1.650	1.638	1.665	1.650	1.641	1.654
β	1.677	1.668	1.662	1.652	1.678	1.664	1.651	1.666
γ	1.683	1.677	1.669	1.661	1.684	1.673	1.664	1.674
$\gamma-\alpha$	0.019	0.024	0.019	0.023	0.020	0.023	0.023	0.020
$Z\wedge c$	15°	16°	17°	18°	19°	17°	22°	19°
$-2V$								
meas.	65°	72°	72°	78°	67°	75°	98°	78°
calc.	68°	74°	74°	78°	68°	77°	98°	78°
Pleochroism*								
X	brn-y	p y	y	p y	y	p y	y	y-grn
Y	y-grn	y-grn	grn	lt grn	grn	lt grn	y-brn	lt grn
Z	d bl-grn	brn-grn	bl-grn	lt bl-grn	bl	bl-grn	lt brn	d grn

* Abbreviations used in color descriptions: y—yellow; bl—blue; grn—green; brn—brown; p—pale; d—deep; lt—light.

The complexity of hornblende composition presents a very definite problem in approximating composition from optical data. In spite of the fact that many of the isomorphous substitutions are interdependent, there still may be as many as five or six factors influencing a particular optical property. With any convenient method it can be hoped only to determine the ratios of a few of the constituents; those which have the strongest effect on the optical properties. Winchell (1945) has tabulated the properties of approximately one hundred calcic amphiboles on a partial triangular prism. There are eight end-member molecules in this system as follows:

$Ca_2Mg_5Si_8O_{22}(OH)_2$
$Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$
$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$
$NaCa_2Mg_5AlSi_7O_{22}(OH)_2$

$Ca_2Fe''_5Si_8O_{22}(OH)_2$
$Ca_2Fe''_3Fe'''_2Al_2Si_6O_{22}(OH)_2$
$NaCa_2Fe''_4Fe'''Al_2Si_6O_{22}(OH)_2$
$NaCa_2Fe_5AlSi_7O_{22}(OH)_2$

In addition to this diagram, a similar one for the oxyhornblendes is given. In any actual case a combination of the two would be necessary since most common hornblende contains some of the oxyhornblende molecule. In the actual plotting of data in this prismatic diagram Winchell combines ferric and ferrous iron and assumes that the calcium content is constant. Combining the irons fails to distinguish their effect, and unless it is assumed that the Fe''/Mg ratio is the same as the Fe'''/Al_y ratio in any one hornblende, the significance of the ferric iron end members is lost. An examination of the data given in Table 3 shows that the assumption is not valid. It is, however, necessary to combine these constituents if we wish to give even an approximate graphical representation of their effect on optical properties. As his four variables Winchell uses the following: (*a*) the number of atoms of silicon minus *6;* (*b*) the number of aluminum atoms in the chain; (*c*) the number of atoms of alkali metals in the vacant position; and (*d*) the ratio of light metals in the Y group to the total Y group ($Mg+Al_y/Y$). The data obtained on the present hornblendes were plotted on Winchell's diagram. The index γ was found to be generally lower than would have been predicted from the diagram; other properties were in good agreement.

Figure 1*b* and 1*c* show the variation of optical properties with increasing $Mg+Al_y/Y$ ratio, that is with decreasing heavy-metal substitution in the Y group. Refractive indices decrease with an increase in this ratio while the optic angle $-2V$ increases. Birefringence measurements are subject to too great an error to be correlated accurately, but this value is generally found to increase with this ratio. It will be noted that the values for sample 35–29 show the greatest deviation from the line drawn as was the case with the specific gravity plot. Increased substitution of aluminum for silicon is probably responsible for this effect. This substitution appears to increase refractive index as well as the optic angle $-2V$.

The transition of the color of hornblendes from brown to green has been discussed in detail by Deer (1938). He has shown that the brown color of ordinary hornblendes is not due to the ferric iron content but rather to titanium. In the oxyhornblendes where the ratio Fe'''/Fe'' rises to values of well over unity the influence of the ferric ion will have a marked effect. In the ordinary hornblendes the value of this ratio is usually below unity and in the present case it is appreciably less. At any given Fe'' content, according to Deer, an increase of Ti should give a browner color in the *Z* direction. A rough correlation between increasing value of the $Fe''/Fe''+Ti$ ratio and a change in color in the Z direction from brown to green is given in Table 6.

Magnetic Properties

During separation by means of the Frantz isodynamic separator, it was noted not all of the hornblendes were removed at the same field intensity. Under the conditions of separation the range in field intensities was very slight, amounting to current changes of less than 0.1 ampere. By changing the angle perpendicular to the feeder trough to 30° rather than 15° this range was spread to about 0.3 ampere. The effect of increasing this

TABLE 6

Sample	Fe''/Fe''+Ti	Color on Z
35-29	0.83	light brown
35-5	0.89	brownish green
35-31	0.90	deep green
35-27	0.92	blue green
35-2	0.92	deep blue-green
35-10	0.93	blue-green
35-22	0.96	blue
35-11	0.97	light blue-green

angle is to make the magnetic field work against gravity to a greater extent. A series of careful measurements were made of the current necessary to deflect each of the hornblendes. The results were plotted against the $Mg+Al_y/Y$ ratio of the hornblende. The current required is inversly proportional to the heavy metal content of the mineral. Such a technique may be useful in approximating the iron or iron plus titanium content of silicate minerals, providing that the conditions of the experiment are kept constant. The data presented in Fig. 2 were obtained under the following conditions: The orientation angles of the trough were 25° parallel, and 30° at right angles; the rate of feed was approximately 1 gram per minute; the current was read at that point where the hornblende was divided equally between the magnetic and non-magnetic fraction.

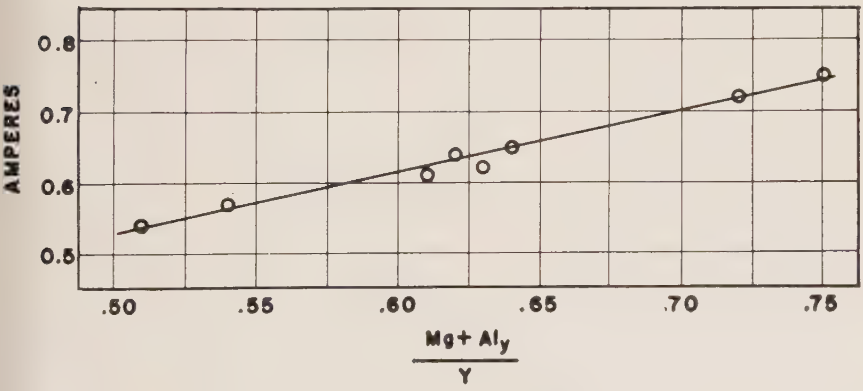


FIG. 2

Genetic Relationships of the Hornblendes

Origin of Hornblendes in General

Hornblendes may originate through either magmatic or metamorphic processes. It is well to restrict magmatic processes to primary crystallization, leaving the alteration of previously formed minerals by residual solutions of magmatic processes to the metamorphic group. Of the hornblendes described here none were formed by purely magmatic processes. The metamorphic processes may be subdivided as follows: (*a*) purely dynamic processes (assuming the necessary water to be already available in the rock); (*b*) contact metamorphic processes, either with or without the addition of new material; (*c*) hydrothermal processes, either with or without the introduction of new material other than water. An examination of these processes shows that there are three factors controlling the composition of the hornblende formed in or from any particular rock type. First, the original composition of the rock; second, the nature of the new materials introduced; and third, the process by which these new materials are added. The greatest proportion of the hornblendes in the Piedmont area were probably formed by hydrothermal or contact processes during large scale regional metamorphism.

A generalized relationship between parent rock and the composition of the hornblende it contains is given by Hallimond (1943). The composition of nearly two hundred hornblendes are plotted on a partial triangular diagram using the number of silicon atoms per cell as one coordinate, the number of aluminum atoms in the chain as the second, and the number of alkali ions in the vacant position as the third. The points for hornblendes occurring in similar tock types were found to lie in certain general fields of the diagram. Hallimond's diorite field includes such rocks as syenites, gabbros and hornblende gneisses. Two fields appear for limestone, one to represent ordinary hornblende and one to represent pargasite. The pargasitic field probably represents those limestones to which material has been added during metamorphism. All of the hornblendes with the exception of 35–29 are closely related to gabbroic rocks or hornblende gneisses, and fall within the diorite or amphibolite fields of Hallimond. The composition of sample 35–29, which occurs in a metagabbro inclusion within limestone, falls in the pargasite field.

Deer (1938) has discussed a group of nine hornblendes from the Glen Tilt complex, Perthshire. In this occurrence xenoliths of hornblendite and hornblende schist are enclosed in rocks of dioritic composition with small patches of appinites. He has shown that the later formed hornblendes show a definite decrease in the Al_2O_3/Fe_2O_3 ratio and an increase in the MgO/FeO ratio. Deer further suggests that the higher the silica content of the rock the higher should be the silica content of the hornblende. In the ensuing discussion it will be demonstrated that under the special conditions of granitization it may be possible for the silica content of hornblende to fall, simultaneously with the increase in silica content of the rock as a whole.

THE GRANITIZATION OF HORNBLENDE ROCKS

The problem of granitization in the Piedmont of south-eastern Pennsylvania has been studied by several workers. The granitization of the Wissahickon formation in general has been discussed by Weiss (1949), and Ch'ih (1950) has dealt specifically with the chemistry of the granitization of the mica schists of this formation. Postel (1938, 1940) has described the granitization of hornblende gneisses associated with the Springfield granodiorite. Granitization of the schists is usually recognized by the appearance of potash minerals such as microcline and biotite. Of the granitization of the gabbroic rocks in the Baltimore gneiss there is little doubt, many of them showing migmatitic facies and distinct signs of assimilation by more felsic rocks.

With the analyses of several hornblendes from such grantized rocks it becomes possible to discuss the effect of granitization processes on this mineral; an aspect of the genesis of hornblende which has received little attention. Since almost all hornblende contains alkalies, which can be present in variable amounts, it is conceivable that the amount of potassium present should increase in hornblendes which have been granitized. An examination of the data in Table 3 shows that the number of potassium atoms in the vacant position AA′ is greatest in those hornblendes from rocks which are known to have been granitized (35-2, -10, -27). The granitization of the Van Artsdalen metagabbro (35-29) has been suggested (Weiss, 1947), and this would be in keeping with the high potash content. No direct reference has been made to the granitization of the metagabbro in the Marshalltown, Delaware area, whose hornblende is also potash rich.

A plot of the potassium atoms per unit cell versus the total sodium atoms per unit cell shows no regular arrangement of points. A plot of the number of potassium atoms per unit cell versus the sodium atoms in the vacant position, however, showed the hornblendes falling into two distinct groups. The hornblendes from rocks showing no obvious signs of granitization (35-5, -11, -22) as well as sample 35-29 fell along a straight line. All of the hornblendes known to be granitized as well as sample 35-31 fell in a group above this line. This suggests that the sodium which replaces the calcium represents an initial alkali content of the hornblende (small amounts of potassium may still be present in the vacant position), and that further addition of alkalies, by whatever process, would introduce them into the vacant position. The ungranitized hornblendes falling on a line represent the addition of potassium and sodium in a certain ratio, the granitized hornblendes falling above this line represent the addition of these elements in a greater ratio to one another. In a true granitization process then, we should expect that the K/Na ratio should rise at the same time that the potassium content increases. Potassium content is plotted versus the ratio K/Na in the vacant position in Fig. 3. The hornblendes fall into two distinct groups. The granitized hornblendes show high potassium with a high K/Na ratio, while the ungranitized hornblendes show a low potassium with a low K/Na ratio.

In his discussion of the Springfield granodiorite Postel (1940) has pointed out several possible sources of granitizing solutions as proposed by earlier workers in this field. They are as follows: (*a*) the hydrolysis of the potash feldspar molecule at the end stages of crystallization to form muscovite and an alkali silicate liquid as shown by Goldschmidt (1922), (*b*) Eskola's (1932) hypothesis of a palingenetic granitic liquid which soaks up into the country rock, and (*c*) a pneumatolitic introduction of granitic material as suggested by MacGregor (1938). Although many more discussions of the origin of granitizing "solutions" are available, these three include the major possibilities. Any one of these processes could introduce potassium into the hornblendes. The following equation (1) illustrates the possible reaction between hornblende and an alkali silicate liquid:

$$(1)\quad \overset{\text{hornblende}}{2Ca_2Mg_4Al_2Si_7O_{22}(OH)_2} + K_2O + \overset{\text{anorthite}}{4CaAl_2Si_2O_8} + H_2O \rightarrow \overset{\text{alk. hornblende}}{2KCa_2Mg_4Al_3Si_6O_{22}(OH)_2} + \overset{\text{epidote}}{2Ca_2Al_3Si_3O_{12}(OH)} + \overset{\text{quartz}}{4SiO_2}$$

Since the silica in the granitizing liquid does not take part in the reaction, it has not been included among the reactants. The anorthite is assumed to be present in the initial rock. This equation suggests a mechanism for the zoisitization of plagioclase. The next equation (2) shows the reaction between hornblende and feldspathic material to give an alkali hornblende and quartz:

$$(2)\quad Ca_2Mg_4Al_2Si_7O_{22}(OH)_2 + KAlSi_3O_8 \rightarrow KCa_2Mg_4Al_3Si_6O_{22}(OH)_2 + 4SiO_2.$$

No attempt is made to illustrate by equations the pneumatolitic introduction of potassium into hornblende.

From both equations it is seen that although silica is introduced, whether as alkali silicate or in a feldspar, the silica content of the hornblende decreases. Some compensation must be made for the introduction of alkali, and the correlation of alkali and aluminum content indicates that this is accomplished by the replacement of silicon by aluminum. Such a process releases silica from the hornblende, which, together with the silica introduced would form quartz. It is possible, then, to decrease the silica content of the hornblende while the silica content of the rock as a whole increases. This is in contradiction with Deer's statement that the silica of hornblende and rock are proportional. The metagabbro in the vicinity of Marshalltown, Delaware (35-11), contains a large amount of quartz and potash-rich hornblende, which possibly illustrates the relationship discussed.

The only possible example of granitization by pneumatolitic processes encountered is the pargasitic hornblende from the metagabbro in the limestone at Van Artsdalen's quarry (35-29). The high fluorine content of the amphibole and the appearance of sodalite in the norms of the associated rocks (Weiss, 1947, p. 830) is suggestive of the influence of gaseous material. This hornblende falls just above the field of ungranitized hornblendes in Fig. 3, that is, it combines a high potassium content with a low K/Na ratio. It is clear that the process of introduction of potassium to this mineral is quite different from that of ordinary granitization. Pneumatolitic granitization might be expected to have different results from that effected by alkali silicate liquids.

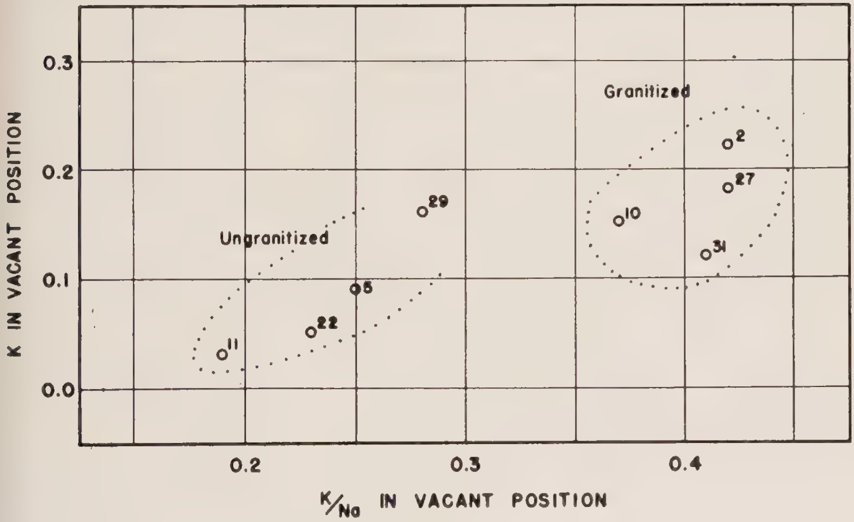


Fig. 3

The most interesting example of granitization of hornblendic rocks is that associated with the formation of the Springfield granodiorite. In this case the hornblende gneisses of the Wissahickon formation have been converted to hornblende-biotite schists with the appearance of large amounts of epidote. The rock types have been described in detail by Postel (1938, 1940). The alkalization of hornblende is necessarily limited especially in the introduction of the large potassium ion, and hence the structure breaks down to form biotite. This conversion of hornblende to biotite is accompanied by the release of large amounts of lime, which must be accounted for. The only minerals into which the lime can go are epidote and sphene. While the sphene content of the rocks increases there is not enough titanium to handle even a major portion of the lime. The quantity of epidote rises locally to form a major portion of the rock and appears to be sufficient to account for all the lime. There is, however, a need for very large amounts of aluminum to form this mineral. Even if the granitizing material is assumed to be feldspathic, the alumina content is too low to combine with all of the lime released from the hornblende. It is possible that the lime freed from the hornblende migrates to those portions of the rock where appreciable anorthite is present and reacts with it to form epidote. This mechanism would account for the extremely high epidote content in some portions of the granitized hornblendic rocks.

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THE STUFFED DERIVATIVES OF THE SILICA STRUCTURES

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ABSTRACT

A *derivative structure* is one derived from a simpler *basic structure* by generalization. This can occur either by distortion of the simpler structure, or by substitutions for its atoms by others of different chemical species. When the substitute atoms have smaller valences than those for which they substitute, this must be compensated by addition of other atoms which can be described as stuffing atoms. Only such atoms as can be accommodated in the available voids of the structure are acceptable stuffing atoms.

This paper treats of the stuffed derivatives of quartz, tridymite, and cristobalite.

Quartz has voids of limited sizes. These are too small for K or Na, but large enough for Li, Be, or B. Eucryptite, $LiAlSiO_4$, and $LiAlSi_2O_6$ are known derivatives of quartz.

Both tridymite and cristobalite have voids large enough to house Na, K, or Ca. The best known derivatives of tridymite are nepheline, $KNa_3Al_4Si_4O_{16}$, and the several forms of $KAlSiO_4$. The compounds $K_2MgSi_3O_8$, $K_2FeSi_3O_8$, and possibly $K_2Mg_5Si_{12}O_{10}$, appear to be derivatives of tridymite in which Mg substitutes for Si.

The cristobalite derivatives include carnegieite, $NaAlSiO_4$, and Na_2CaSiO_4. It seems likely that Na_2MgSiO_4 and Na_2BeSiO_4 may also assume tridymite-like structures.

Non-silicate derivatives of silica are briefly discussed.

BACKGROUND

To appreciate some of the features of the stuffed derivatives of the silica structures it is necessary to understand the technical crystallographic meaning of "derivative," and some of the characteristics of the structures of the various forms of pure silica.

Derivative Structures. There exists a class of crystal structures which are derived from others by generalization. Such a derived structure is known as a *derivative structure*,[1] and it is derived by generalization of a *basic structure.* The symmetry of the derivative structures is a subgroup of the symmetry of the basic structure. Thus, in passing from the basic to the derivative structure there is a loss of symmetry in a given volume. This can be caused physically (a) by distortion of the basic structure, giving rise to a *distortion structure*, or (b) by substitution of different atoms for equivalent atoms in the basic structure, giving rise to a *substitution structure.*

Relations among the Structures of Pure Silica. Pure silica exists in three essentially different kinds of structures. The structures can be readily described in terms of their common structural unit, namely, a cluster of four oxygen atoms tetrahedrally surrounding a silicon atom. This unit is referred to briefly as a tetrahedron. The three kinds of silica comprise three different ways of linking the tetrahedra together by joining them vertex to vertex. Each vertex of a tetrahedron which is joined causes the oxygen of that vertex to be shared between two tetrahedra. When this occurs, only half of the shared oxygen may be said to belong to each of the neighboring tetrahedra. All three forms of silica are characterized by the sharing of all four vertices of all tetrahedra. The formula of the tetrahedron is therefore varied from the formula SiO_4 (for an isolated tetrahedron) to $SiO_{4/2} = SiO_2$ for the silica structures. The particular kind of linking is such that the tetrahedra are strung together in space networks in all three silica structures.

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[1] Buerger, M. J., Derivative crystal structures: *J. Chem. Phys.*, **15**, 1–16 (1947).

The three structural linkages correspond with the minerals cristobalite, tridymite and quartz. The idealized and most symmetrical linkage of tetrahedra in each of these arrangements is a high-temperature form. Each of these can be distorted to form a low-temperature form. The low-temperature forms are accordingly derivative structures, specifically distortion structures. In tridymite there are two distorted forms, known as middle-tridymite and low-tridymite. The natures of the distortions in these last two structures have not been determined in detail. Barth[2] has also examined the structure of high-cristobalite below its range of true stability (i.e., in the region of stability of high-tridymite) and found it somewhat distorted from the ideal structure[3,4]. Thus, the unstable structures may be derivative structures by distortion.

Chemical Basis of Stuffing. If, during the formation of a silica structure, a certain porportion of the Si^{++++} atoms is replaced by Al^{+++} atoms (which can also assume a coordination number four with respect to oxygen) the total valence of the metals in the structure is reduced in proportion to the number of substitutions. This loss of valence of the metals can be counterbalanced by addition of other metal atoms to the structure. In fact, if an Al^{+++} substitutes for a Si^{++++}, the field caused by the deficiency of positive charge forms a negatively charged site which attracts positive ions. The field is locally neutralized when the charge on the attracted ion just equals that of the average deficiency of the region. Taking coordination into account, the alkali and alkaline earth ions neatly perform the function of neutralizers. Naturally, these extra atoms must find space accommodation in the structure.

A list of the known stuffed derivatives of the silica structures is given in Table 1.

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[2] Barth, Tom F. W., The cristobalite structures. I. High cristobalite: *Am. Jour. Sci.*, **23,** 350–356 (1932).

[3] Nieuwenkamp, W., Die Kristallstruktur des Tief-Cristobalits SiO_2: *Zeit. Krist.*, **A 92,** 82–88 (1935).

[4] Nieuwenkamp, W., Über die Struktur von Hoch-Cristobalit: *Zeit. Krist.*, **A 96,** 454–458 (1937).

Table 1. Stuffed Derivatives of the Silica Structures

Basic Structure	Derivative Structure	Space Group
High quartz		$C6_32$
	(low-quartz	$C3_12$)
	$LiAlSiO_4$ high eucryptite	$C6_32$? or $C2$?
High tridymite		$C\frac{6_3}{m}\frac{2}{m}\frac{2}{c}$ ($C6/mmc$)
	$BaAl_2O_4$ $SrAl_2O_4$ $BaFe_2O_4$ $SrFe_2O_4$ $PbFe_2O_4$	$C6_32$
	$KLiSO_4$ $KAlSiO_4$ (kalsilite)	$C6_32$
	$KAlSiO_4$ (kaliophilite)	$C6_32$?
	$KAlSiO_4$ (orthorhombic)	?
	$K_2MgSi_3O_8$	?
	$K_2FeSi_3O_8$	?
	$K_2Mg_5Si_{12}O_{30}$	?
	$KNa_3Al_4Si_4O_{16}$ (nepheline)	$C6$
High cristobalite		$F\frac{4_1}{d}\bar{3}\frac{2}{m}$ ($Fd3m$)
	Barth's high cristobalite Barth's $NaAlSiO_4$, (high-carnegieite) Barth's $NaCaSiO_4$ Barth's $Na_2Al_2O_4$ Barth's $K_2Al_2O_4$ Barth's $K_2Fe_2O_4$ Barth's $Rb_2Fe_2O_4$ Barth's $PbFe_2O_4$	$P2_13$

QUARTZ-LIKE STRUCTURES

The structure of quartz is so tight that very limited space exists for the housing of extra stuffing atoms. Li^+, and presumably Be^{++} and B^{+++} are small enough to fit into the interstitial spaces of the quartz structure.

It is known that Li^+ can be drawn through the interstices of quartz at high temperatures with the aid of an electric field, but the larger alkalis Na^+ and K^+ cannot.[5] In accordance with this one might expect crystals of the type

$$\mathrm{Li}_x \left| \begin{matrix} \mathrm{Al}_x \\ \mathrm{Si}_{1-x} \end{matrix} \right| \mathrm{O}_2, \text{ possibly } \mathrm{Be}_{x/2} \left| \begin{matrix} \mathrm{Al}_x \\ \mathrm{Si}_{1-x} \end{matrix} \right| \mathrm{O}_2, \text{ and } \mathrm{B}_{x/3} \left| \begin{matrix} \mathrm{Al}_x \\ \mathrm{Si}_{1-x} \end{matrix} \right| \mathrm{O}_2.$$

Conceivably similar stuffed structures could be based upon the quartz-like GeO_2 structure.

Actually lithium is known to stuff the quartz structure. During the war Winkler[6] incidentally synthesized eucryptite,

$$\mathrm{Li}_{1/2} \left| \begin{matrix} \mathrm{Al}_{1/2} \\ \mathrm{Si}_{1/2} \end{matrix} \right| \mathrm{O}_2 = \tfrac{1}{2}\,\mathrm{LiAlSiO}_4$$

while preparing artificial nepheline. He later studied the structure of this material,[7] chiefly with the aid of powder photographs. He concluded that it had a high-quartz type structure in which Al atoms substitute for half the Si atoms of the quartz structure in alternate layers along the c axis. The Li atoms are in the interstitial space on the level where the substitution takes place, surrounded by four oxygen atoms. This arrangement has a very satisfactory Pauling electrostatic bond structure. The oxygens surrounding the Li are shared by one Si and one Al, so that they receive electrostatic bonds of strength $1\frac{3}{4}$ from this source. The tetrahedrally coordinated Li atoms contribute the remaining $\frac{1}{4}$.

Crystals similar to those described by Winkler were prepared in the Washken Laboratory[8] following Winkler's directions.[6] Before the appearance of Winkler's structure determination, the crystals were independently recognized as being of the quartz-type because of their habit (which resembles the high-quartz phenocrysts of quartz porphyries) and because their x-ray powder patterns and rotating crystal patterns resemble the quartz patterns.[8] An x-ray examination by Buerger[8,9] by powder, rotating-crystal, and precession methods revealed not only a doubled c axis discovered by Winkler, but a doubled a axis as well. In this respect, and in respect to the appearance of reflections 000*l* in all orders (Buerger, but not Winkler), the results differ from Winkler's results, and suggest a monoclinic symmetry. Comparison of the Winkler and Buerger data are summarized in Table 2.

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[5] Harris, P. H., and Waring, C. E., Diffusion of lithium ions through quartz in an electric field: *J. Phys. Chem.*, **41**, 1077–1085 (1937).

[6] Winkler, Helmut G. F., On the synthesis of nepheline: *Am. Mineral.*, **32**, 131–136 (1947).

[7] Winkler, Helmut G. F., Synthese und Kristallstruktur des Eukryptits, $\mathrm{LiAlSiO}_4$: *Acta Cryst.*, **1**, 27–34 (1948).

[8] Washken, Edward, Investigation of nepheline and related substances with particular emphasis on growing crystals for piezoelectric measurements. Contract **No. 2 36-039 sc-32333**. Quarterly interim report to the *U. S. Signal Corps*, No. **15** (15 April, 1948).

[9] Buerger, M. J., Crystals based on the silica structures: *Am. Mineral.*, **33**, 751–752 (1948).

TABLE 2

	Low Quartz	High Quartz	Eucryptite	
			Winkler[7]	Buerger[8,9]
a	4.913 Å	5.02	5.27	2×5.275
c	5.404	5.48	2×5.625	2×5.61
c/a	1.10	1.09	2×1.067	1.064
cell content	3 SiO_2	3 SiO_2	3 $LiAlSiO_4$	6 $LiAlSiO_4$
space group	$C3_12$	$C6_22$	$C6_22$	$P2$ probably
density	2.649	2.518 at 600° C.	2.352 actual 2.305 x-ray	2.305 actual 2.30 x-ray

It is difficult to understand the divergence of Winkler's and Buerger's data. Winkler's structure is so obvious that one would not ordinarily doubt it. On the other hand, Buerger's data were obtained by the more powerful rotating-crystal and precession methods. Unfortunately only one crystal was so examined. The investigation should be repeated on other crystals for checking purposes.

It is possible that various degrees of disorder or deviation in formula can occur in eucryptite which would reconcile Winkler's and Buerger's data. Roy and others[10,11] have investigated the system eucryptite-silica. They have shown that a considerable range of composition can occur in eucryptite.

Gruner[12] has also given a brief statement that a form of

$$LiAlSi_2O_6 = 3\ Li_{1/3} \left| \begin{matrix} Al_{1/3} \\ Si_{2/3} \end{matrix} \right| O_2$$

(which is the same composition as that of the mineral spodumene) has a structure which is a derivative of the quartz structure.

OPEN STRUCTURES WITH LIMITED STUFFING

Cristobalite and tridymite occur as minerals under circumstances which rule out their formation as stable structures of silica. Long ago it

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[10] Roy, Rustom, and Osborn, E. F., The system lithium metasilicate-spodumene-silica: *J. Am. Chem. Soc.* **71,** 2086–2095 (1949).

[11] Roy, Rustom, Roy, Della M., and Osborn, E. F., Compositional and stability relations among the lithium aluminosilicates: eucryptite, spodumene, and petalite. *J. Am. Ceram. Soc.*, **33,** 152–159 (1950).

[12] Gruner, J. W., Progress in the silicate structures: *Am. Mineral.*, **33,** 679–691 (1948).

was pointed out[13] that the available analyses of such natural tridymite and cristobalite always contain small amounts of elements other than silicon and oxygen, including some large atoms of the alkali and alkaline earth groups. Evidently the large atoms can be housed in the interstitial spaces of the more open structures of tridymite and cristobalite, but cannot be accommodated in the structure of quartz. Conversely, a crystal which grows in such a way that it includes the elements shown by the analyses cannot have the quartz structure, but could only have the tridymite or cristobalite structures. The presence of the additional elements extends the temperature ranges of the open structures downward at the expense of the range of the tighter quartz structure.

More recently a specific case[14] of this was examined in the Mineralogical Laboratory of the Massachusetts Institute of Technology. The tridymite from Las Plumas County, California, was found to be based upon one of the orthorhombic space groups $F222$, Fmm, or $Fmmm$, with a comparatively large cell of dimensions

$$\begin{aligned} a &= 9.91\ \text{Å} \\ b &= 17.18 \\ c &= 81.57 \end{aligned}$$

Chemical and spectroscopic examination showed a small content of non-silica elements, the formula being approximately $NaCaAl_3Si_{15}O_{36}$.

Pure silica tridymite has transformations at 117° C. and 163° C. The Las Plumas tridymite has only one inversion at 127° C., directly from the low form to a high form which gives the x-ray reflections of the ordinary high-tridymite cell, plus some additional reflections whose characteristics vary non-reversibly with time. There is no middle tridymite form in this material.

The tridymite from San Cristobal, Mexico, has the same a and b axes as the Las Plumas material, but has only half as long a c axis. It inverts from the low form to the high form in two stages, but not at 117° C. and 163° C. as in pure silica tridymite. The inversion points occur at 121° C. and 135° C. The variation in inversion temperature must be a function of impurity with respect to pure silica as standard. The range of stability of middle tridymite would appear to become narrower with increasing impurity.

Barth and Kvalheim[15] subsequently but independently discovered the same situation in natural tridymite from Deception Island in the Antarctic Archipelago. This tridymite has greater refractive indices than pure tridymite by about 0.01. The Deception Island tridymite inverts directly from the low form to the high form at about 135° C., with some variation between samples, but always between 130° C. and 140° C. Spectroscopic analyses showed that this material has a composition lying between that of silica and nepheline, specifically about 5% nepheline, 95% silica, i.e.

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[13] Buerger, M. J., The silica framework crystals and their stability fields: *Zeit. Krist.*, **A 90**, 186–192 (1935).

[14] Buerger, M. J., and Lukesh, Joseph, The tridymite problem: *Science*, **95**, 20–21 (1942).

[15] Barth, Tom F. W., and Kvalheim, Aslak, Christensenite, a solid solution of nepheline in tridymite: *Norske Videnskaps Akademi i Oslo*, **No. 22** (1944).

$$\frac{NaAlSiO_4}{SiSiO_4} = \frac{5}{95}$$

This suggests a formula approximately $NaAlSi_{49}O_{100}$.

Tuttle[16] has recently discovered small variations in the high-low transformation of quartz near 573° C., which may be attributed to small amounts of impurity.

The evidence presented in this section makes it plain that tridymite has been formed in nature, presumably by hydrothermal synthesis, which has small amounts of Al replacing Si atoms of the pure silica structure, and also small amounts of alkali or alkaline earth atoms. The latter are doubtless present in the large interstitial spaces of the tridymite structure and are responsible for the assumption of the tridymite structure by this group of atoms rather than the tighter quartz structure, which would be the stable form of pure silica under the conditions of formation.

Stuffed Derivatives of Tridymite

The most important derivatives of tridymite have compositions in the range $NaAlSiO_4$-$KAlSiO_4$. The relations between the various species of these crystals are by no means entirely clear.

Nepheline. Schiebold[17] first suggested that nepheline has a tridymite-like structure, with half the Si atoms replaced by Al, and with Na in the interstices to balance the valence. This structure was merely a suggestion and was not supported by an intensity study. Buerger, Klein, and Hamburger[18] made a detailed *x*-ray investigation of nepheline and were led to a structure essentially the same as the structure suggested by Schiebold. This distribution of atoms of this structure with respect to the symmetry elements is such that the alkalis are clearly separated into two categories, so that the formula of nepheline is $A' A_3'' Al_4Si_4O_{16}$. The structure is based upon a tridymite structure somewhat collapsed by a rotational distortion of the silica framework. The type of collapse is such that the void in which A' is situated is large while that within which A'' is situated is smaller. Since analyses of natural nepheline[19] show the presence of both potassium and sodium in a ratio which ranges in the neighborhood of 1:3, it is obvious that the natural formula for nepheline is not simple $NaAlSiO_4$, but rather $KNa_3Al_4Si_4O_{16}$.

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[16] Tuttle, O. F., The variable inversion temperature of quartz as a possible geological thermometer: *Am. Mineral.*, **34**, 723–730 (1949).

[17] Schiebold, E., Zur Struktur von Nephelin und Analcim: *Naturwiss.*, **18**, 705–706 (1930).

[18] Buerger, M. J., Klein, Gilbert, and Hamburger, Gabrielle, The structure of nepheline: *Am. Mineral.*, **32**, 197 (1947).

The structure of nepheline is being refined by Theo Hahn and M. J. Buerger. A detailed account of the structure determination is expected shortly.

On the basis of this rational formula, Washken and Buerger[20] synthesized "rational" nepheline. This proved to crystallize directly from the melt, in contrast with the arbitrarily pure composition $NaNa_3Al_4Si_4O_{16} = 4\ NaAlSiO_4$, which, when crystallized from the melt, assumes the carnegieite form, which has a stuffed cristobalite structure.[31] This clearly shows that results of phase diagram investigations which include a nepheline phase should not necessarily be applied to all compositions having the nepheline structure.

Generally speaking, phase diagram results obtained in the melt-crystal region should not be regarded as fixing the natures of the phase fields involving crystalline phases at lower temperatures. This became obvious[21] when it was found that, although the plagioclase crystals are the classical examples of complete solid solutions at high temperatures as they precipitate from the melt, they certainly do not form complete solid solutions at low temperatures. The same is doubtless true in the system $NaAlSiO_4$-$KAlSiO_4$. Thus, Bowen[22] found a complete series of solid solutions in this system between "nepheline" and "kaliophilite." But it does not follow that the phases stable at low temperatures form this complete series of solid solutions. Incidentally, Bowen's diagram shows an interesting singularity even at high temperatures at about the ideal nepheline composition $KNa_3Al_4Si_4O_{16}$.

Recently Wyart has synthesized nepheline hydrothermally.[23] The raw

[19] Banister, F. A., and Hey, M. H., A chemical, optical, and x-ray study of nepheline and kaliophilite: *Mineral. Mag.*, **22**, 569–608 (1931).

[20] Washken, Edward, and Buerger, M. J., The effect of potassium on the nepheline-carnegieite transformation: *Am. Mineral.*, **35**, 290–291 (1950).

[21] Buerger, M. J., The role of temperature in mineralogy: *Am. Mineral.*, **33**, 101–121 (1948), especially pages 118–121.

[22] Bowen, N. L., The sodium-potassium nephelites: *Am. Jour. Sci.*, **43**, 115–132 (1917).

[23] Wyart, Jean, and Michel-Lévy, Mireille, Cristallisation du mélange $N_xK_{1-x}AlSiO_4$ en présence d'eau sous pression (formation de nepheline, kalsilite, hydrocancrinite, hydrosodalite, mica): *Compte Rend.*, **229**, 131–133 (1949).

materials were NaOH, KOH, Al_2O_3, and SiO_2, which were placed in closed red copper tubes and heated in a small autoclave. Nepheline prisms up to .080 mm. long were obtained at 415° C. which had a composition $Na_{1-x}K_xAlSiO_4$, where x is in the neighborhood of 0.2–0.3. Note that this composition corresponds with that deduced from the crystal structure analysis carried out in the Mineralogical Laboratory of the Massachusetts Institute of Technology.

The Forms of $KAlSiO_4$. The compound $KAlSiO_4$ appears to occur in three modifications, two hexagonal and one orthorhombic. The two hexagonal forms correspond to the minerals kaliophilite and kalsilite.[24] Some characteristic properties of these forms are shown in Table 3. Some data for high tridymite and nepheline are added for comparison.

TABLE 3

	Space Group	Cell Edges			Refractive Indices		Specific Gravity
		a	$a\sqrt{3}$, or b	c	ω (or γ)	ϵ (or α)	
Kaliophilite	$C\,6_32$?	26.9	46.7	8.55	1.530	1.526	2.606
Kalsilite	$C\,6_32$	5.17	8.96	8.67	1.542	1.537	2.59
Ortho $KAlSiO_4$	?	9.00	15.68	8.53	1.536	1.528	2.60
Tridymite	$C\,\frac{6}{m}\,\frac{2}{m}\,\frac{2}{c}$	5.03	8.70	8.22			
Nepheline	$C\,6_3$	9.99	17.3	8.39	1.544	1.539	2.65

It will be observed that kalsilite has a cell approximately the same as that of high-tridymite. Claringbull and Bannister[25] have shown that this mineral has indeed a structure which is a very simple derivative of the high-tridymite structure. Half the silicon atoms are replaced by aluminum atoms and the large interstices of this $(AlSiO_2)^{-1}$ net house the K^+ ions. The structure is very similar to that of the $BaAl_2O_4$ structure discussed in Appendix I.

The structure of the mineral kaliophilite is unknown. Bannister and Hey[19] have pointed out that the axes of kaliophilite are closely related to those of tridymite. These minerals have the same c axis length and the kaliophilite a axis is about $3\sqrt{3}$ times the a axis of high tridymite, i.e. about 3 times the long diagonal of the tridymite hexagonal unit cell. This close geometrical relation, the relation between chemical formulae and the similarity in densities and refractive indices of kaliophilite and nepheline make it very probable that kaliophilite has a structure which is a derivative of that of high-tridymite.

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[24] Bannister, F. A., and Hey, Max H., Kalsilite, a polymorph of $KAlSiO_3$, from Uganda: *Mineral. Mag.*, **26**, 218–224 (1942).

[25] Claringbull, C. F., and Bannister, F. A., The crystal structure of kalsilite: *Acta Cryst.* **1**, 42 (1948).

Lukesh and Buerger[26] determined the space group of kaliophilite as $C6_32$ on the assumption that the material which they had was a single crystal. Although this material was as good as it was possible to obtain, there is a strong possibility that the material was twinned, in which case the symmetry may be lower than $C6_32$. For example, kaliophilite could actually be orthorhombic.

The structure of orthorhombic $KAlSiO_4$ is unknown. Table 3 shows that its *a* axis is about equal to the cell diagonal of kalsilite, its *b* axis is twice the *a* axis of kalsilite, and the *c* axes of the two crystals are about the same. From this relation and the similar refractive indices it is likely that the structure of kalsilite is also a derivative of that of high-tridymite.

The stability relations between these three forms of $KAlSiO_4$ have been investigated by Rigby and Richardson.[27] Their experimentation with melts suggests that kaliophilite is a low-temperature form and that the orthorhombic form is a high-temperature one. The inversion boundary between them is in the neighborhood of 900° C. Kalsilite requires a small percentage (1.5–5%) of Na_2O to form. Depending on the Na content, kalsilite inverts to the orthorhombic form at temperatures from 1300° C. to 1500° C. Schaierer[28] confirmed that the high-temperature form of $KAlSiO_4$ is the orthorhombic modification. This can accept considerable Na in place of K. Wyart[29] synthesized kalsilite hydrothermally at temperatures up to 500° C. This was accomplished in the absence of soda, using silica, amorphous alumina, and a solution containing potassium.

It will be noted in passing that Bowen's conclusions[22] regarding the continuous series of solid solutions between nepheline and kaliophilite appear to be in error. Nepheline has a cell which is different from that of any of the three forms of $KAlSiO_4$. This emphasizes the danger of extrapolating data which determine liquidus curves into the field of the lower-temperature crystalline phases.

Tridymite-Like Potassium Magnesium Silicates. Roedder[30] has discovered at least one tridymite-like compound in investigating the system K_2O-MgO-SiO_2. The compound

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[26] Lukesh, Joseph S., and Buerger, M. J., The unit cell and space group of kaliophilite: *Am. Mineral.*, **27**, 226–227 (1942).

[27] Rigby, G. R., and Richardson, H. M., The occurrence of artificial kalsilite and allied potassium aluminum silicates in blast-furnace linings: *Mineral. Mag.*, **28**, 75–87 (1947).

[28] Schairer, J. F., The alkali-feldspar join in the system $NaAlSiO_4$-$KAlSiO_4$-SiO_2: *Jour. Geol.*, **58**, 512–517 (1950).

[29] Wyart, Jean, Synthése de la kalsilite et de l'orthose: *Compte Rend.*, **225**, 944–946 (1947).

[30] Roedder, Edwin Woods, The system K_2O—MgO—SiO_2: *Am. J. Sci.*, **249**, 81–130, and 224–248 (1951).

$$K_2O \cdot MgO \cdot 3SiO_2 = K_2MgSi_3O_8 = 2K \left| \begin{matrix} Mg_{1/2} \\ Si_{1\,1/2} \end{matrix} \right| O_4$$

can also be written

$$K_{1/2} \left| \begin{matrix} Mg_{1/4} \\ Si_{3/4} \end{matrix} \right| O_2$$

to bring out its relation to the SiO_2 formula. This occurs in two forms designated α and β. The α form is obtained directly from melts, has a hexagonal outline and a uniaxial interference figure. Nevertheless the platelets bear certain groves which suggest twinning of a less symmetrical structure than hexagonal. The powder pattern is very similar to that of kalsilite. The structure, therefore, is undoubtedly that of a stuffed tridymite-like kalsilite in which, curiously enough, the comparatively large Mg atom substitutes for $\frac{1}{4}$ of the Si atoms in the network. This phase tends to invert spontaneously but slowly to a fibrous form which has been designated β.

Later Roedder[30a] discovered the compound $K_2O \cdot FeO \cdot 3SiO_2 = K_2FeSi_3O_8$ in the system K_2O-FeO-SiO_2. This melts congruently near 900° C. Its mean refractive index is about 1.575 with a birefringence of 0.01. Some of the individual crystals are definitely uniaxial negative, and powder photographs are nearly identical with those of the magnesium analog. The formula can therefore be interpreted as tridymite-like, or as

$$K_{1/2} \left| \begin{matrix} Fe_{1/4} \\ Si_{3/4} \end{matrix} \right| O_2.$$

Roedder[30] also encountered a phase having the composition $K_2O \cdot 5MgO \cdot 12SiO_2 = K_2Mg_5Si_{12}O_{30}$ which crystallizes in thin hexagonal plates having uniaxial optical properties with $\omega = 1.543$, $\epsilon = 1.550$. These properties suggest a tridymite-like structure. If so, the structure can be fitted to a silica-like formula as follows:

$$K_2Mg_5Si_{12}O_{30} = \left| \begin{matrix} K_2 \\ Mg_{\frac{2}{4}} \end{matrix} \right| \quad \left| \begin{matrix} Mg_3 \\ Si_{\frac{12}{15}} \end{matrix} \right| O_{30}.$$

STUFFED DERIVATIVES OF CRISTOBALITE

Barth and Posnjak[31–33] have shown that two silicates have structures which are stuffed derivatives of cristobalite. These are the high-carnegieite form of $NaAlSiO_4$, and Na_2CaSiO_4.

[30a] Roedder, Edwin, A reconnaissance of liquidus relations in the system $K_2O \cdot 2SiO_2$—FeO—SiO_2: *Am. Jour. Sci.*, 435–456 (1952).

[31] Barth, Tom F. W., and Posnjak, E., Silicate structures of the cristobalite type I. The crystal structure of carnegieite ($NaAlSiO_4$): *Zeit. Krist.*, **81**, 135–141 (1932).

[32] Barth, Tom F. W., and Posnjak, E., Silicate structures of the cristobalite type II. The crystal structure of Na_2CaSiO_4: *Zeit. Krist.*, **81**, 370–375 (1932).

[33] Barth, Tom F. W., and Posnjak, E., Silicate structures of the cristobalite type III. Structural relationships of high-cristobalite, α-carnegietic and Na_2CaSiO_4: *Zeit. Krist.*, **81**, 376–385 (1932).

Carnegieite. Bowen and Grieg's early investigation[34] of the phases of $NaAlSiO_4$ showed that, whereas nepheline is the stable form below 1248° C., the form stable just above this temperature is an isometric form known as carnegieite. Nepheline and carnegieite are separated by a sluggish transformation. If the form of carnegieite stable just above this transformation point is cooled past 1248° C. and not allowed time to invert, it suffers another rapid and reversible transformation at 690° C. to a birefringent form. The forms above and below this rapid inversion may be designated high- and low-carnegieite respectively.

Barth and Posnjak[31] investigated the structure of high-carnegieite by the powder method and found it to be a stuffed derivative of cristobalite in which a network of composition $(AlSiO_4)^{-1}$ assumes the structural role of the pure silica network of cristobalite, and in which Na^+ ions occupy half the voids in the network.

Barth and Posnjak's structure[31] has the symmetry $P2_13$, which is a derivative symmetry of that of high-cristobalite,

$$Fd3m = F\frac{4_1}{d}\,\bar{3}\,\frac{2}{m}\cdot$$

Unfortunately, these investigators determined this structure from x-ray diffraction data secured at about 750° C. Although this temperature is above that of the inversion to low-carnegieite, it is below that of the nepheline inversion, 1248° C. The crystals were therefore unstable and in a condition known as a stranded phase [13,35]. The symmetry $P2_13$ is doubtless correct for this condition, but the writer believes that the structure would have a higher symmetry if examined in its true stability range above 1248° C. This is essentially the same comment which was made above in connection with the relation between Barth's[2] unsymmetrical high-cristobalite structure as compared with Nieuwenkamp's symmetrical one.

Na_2CaSiO_4. Barth and Posnjak[32,33] also investigated the structure of the artificial compound Na_2CaSiO_4 and found it to be a derivative of the high-cristobalite structure. The silica network is replaced by one of composition $(CaSiO_4)^{-2}$ and the 2 Na^+ ions completely fill the larger voids of the network. The structure is substantially the same as that of carnegieite except that the replacement Ca^{2+} for Al^{3+} in the network increases the negative charge on the net so that two Na^+ ions are required for neutralization.

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[34] Bowen, N. L., and Greig, J. W., The crystalline modifications of $NaAlSiO_4$: *Am. J. Sci.*, **10,** 204–212 (1925).

[35] Buerger, M. J., The general rôle of composition in polymorphism: *Proc. Nat. Acad. Sci.*, **22,** 685–689 (1936).

In this network the Ca^{2+} ions have four coordination, which is unusual, because the large radius of Ca^{2+} ordinarily requires a coordination of six to nine oxygen atoms. The tetrahedral coordination could be more reasonably expected for the two smaller alkaline earth ions Mg^{2+} and Be^{2+}. For this reason the writer believes it likely that the compounds Na_2MgSiO_4 and Na_2BeSiO_4 may also assume this structure.

APPENDIX I

Nonsilicates with Silica-Like Structures

There are a number of compounds which contain no silica and which, therefore, could not possibly be termed stuffed derivatives of the silica structures in the strict sense, but which nevertheless have structures which are similar to such structures. These are chiefly aluminates and ferrates of tridymite and cristobalite types.

Tridymite-Like Nonsilicates

Barium-Aluminate-Type Structures. The structure of $BaAl_2O_4$ was established by Wallmark and Westgren.[36] They heated mixtures of various proportions of BaO and Al_2O_4 in platinum crucibles over a gas flame and examined the reaction products by the x-ray powder method. They deduced a hexagonal structure which has Al and O atoms arranged as the Si and O atoms in the high-cristobalite structure, with the Ba atoms in the interstitial spaces. Similar structures were found for $SrAl_2O_4$, $BaFe_2O_4$ $SrFe_2O_4$ and $PbFe_2O_4$. These structures are essentially the same as that of hexagonal $KAlSiO_4$, kalsilite.

All these structures are open to the objection that they were investigated by the comparatively weak powder method which is very insensitive to symmetry. Though the general features of the structures are doubtless correct, there remains a chance that they may, in fact, be less symmetrical.

Potassium-Lithium-Sulfate-Type Structures. The structure of $KLiSO_4$ was analyzed many years ago by Bradley[37], who used powder and spectrometer methods. The structure is of the general tridymite type. Li and S atoms substitute for Si, and K^+ fills the large voids in the $(LiSO_4)^{-1}$ network. This structure is exactly isotypic with the kalsilite form of $KAlSiO_4$.

Cristobalite-Like Nonsilicates

Barth[38] studied the compounds $K_2Al_2O_4$, $K_2Fe_2O_4$ and $Na_2Al_2O_4$ and found them all to have powder photographs similar to those of the cristobalite derivatives such as Na_2CaSiO_4. Barth also pointed out that from the data provided by Hilpert and Lindner,[39] it could be deduced that $Rb_2Fe_2O_4$ and $PbFe_2O_4$ also have similar structures.

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[36] Wallmark, Signe, and Westgren, A., *X*-ray analysis of barium aluminates: *Arkiv. för Kemi. Min. och Geol.*, **1213,** No. 35 (1937).

[37] Bradley, A. J., The crystal structure of lithium potassium sulfate: *Phil. Mag.*, **49,** 1225–1237 (1935).

[38] Barth, Tom F. W., Non-silicates with cristobalite-like structure: *J. Chem. Phys.*, **3,** 323–325 (1935).

APPENDIX II

TRIDYMITE VERSUS CRISTOBALITE STRUCTURES

It is interesting to compare lists of compounds having the tridymite and cristobalite structures. Such lists are shown in Table 4. From this it is evident that, except for $PbFe_2O_4$ and high-$NaAlSiO_4$, all compounds with a single stuffing atom assume a tridymite-like structure, while those with two stuffing atoms assume cristobalite-like structures.

TABLE 4. COMPOUNDS ASSUMING TRIDYMITE-LIKE AND CRISTOBALITE-LIKE STRUCTURES

Tridymite-Like Structures	Cristobalite-Like Structures
$\mathrm{K}\left\vert\begin{matrix}\mathrm{Li}\\\mathrm{S}\end{matrix}\right\vert\mathrm{O_2}$	
$\mathrm{Rb}\left\vert\begin{matrix}\mathrm{Li}\\\mathrm{S}\end{matrix}\right\vert\mathrm{O_2}$	
$\text{low-Na}\left\vert\begin{matrix}\mathrm{Al}\\\mathrm{Si}\end{matrix}\right\vert\mathrm{O_2}$	$\text{high-Na}\left\vert\begin{matrix}\mathrm{Al}\\\mathrm{Si}\end{matrix}\right\vert\mathrm{O_2}$
$\mathrm{K}\left\vert\begin{matrix}\mathrm{Al}\\\mathrm{Si}\end{matrix}\right\vert\mathrm{O_2}$	$\mathrm{Na_2}\left\vert\begin{matrix}\mathrm{Ca}\\\mathrm{Si}\end{matrix}\right\vert\mathrm{O_2}$
$Ba\ Al_2O_4$	$Na_2Al_2O_4$
$Sr\ Al_2O_4$	$K_2Al_2O_4$
$Pb\ Al_2O_4$	
$Ba\ Fe_2O_4$	$K_2Fe_2O_4$
$Sr\ Fe_2O_4$	$Rb_2Fe_2O_4$
$Pb\ Fe_2O_4$	$Pb\ Fe_2O_4$

This observation can be rationalized. With one void stuffed, a collapse of the network is permitted provided that the network is the hexagonal tridymite network. Such a collapse, which consists of a rotation of tetrahedra about the hexagonal axis, is such as to offer better coordination to the stuffing ions. On the other hand, with two voids stuffed, the net could collapse very little indeed. In such an event the hexagonal network is no longer the favored one. The question is, why is the isometric (cristobalite) network assumed. It would appear that the greater symmetry of the isometric network makes it a more probable structure, and therefore one more likely to be assumed by the atoms in question. This is also the reason for the assumption of the more symmetrical network by the high-temperature forms such as high-cristobalite itself and high-carnegieite. Furthermore, in the higher temperature stuffed structures, the stuffing atoms doubtless flow through the voids of the network in interstitial disorder. The flow is easier in the more symmetrical network.

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[39] Hilpert, S., and Lindner, A., Über Ferrite. 2. Metteilung: Gruppe der Alkali-, Erdalkali- und Bleiferrite: *Zeit. f. physik. Chemie*, **B22**, 395–405 (1933).

Table 5. Tridymite-Like Crystals with Fractional Amounts of Stuffing Atoms

$K_{1/4}$ $Na_{3/4}$	Al_1 Si_1	O_2	ideal nepheline
$Na_{1/18}$ $Ca_{1/18}$	$Al_{1/6}$ $Si_{5/6}$	O_2	Las Plumas tridymite
$Na_{.2}$	$Al_{.2}$ $Si_{.98}$	O_2	christensenite
$K_{1/2}$	$Mg_{1/4}$ $Si_{3/4}$	O_2	compounds produced by Roedder[30,30a]
$K_{1/2}$	$Fe_{1/4}$ $Si_{3/4}$	O_2	
$K_{2/15}$ $Mg_{2/15}$	$Mg_{1/5}$ $Si_{4/5}$	O_2	

Table 5 lists some tridymite-like crystals discussed in the text in which the stuffing atoms occur in fractional amounts, based upon an SiO_2 formula. These compounds also comform to the discussion just given.

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HACKMANITE AND ITS TENEBRESCENT PROPERTIES

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Abstract

A brief review of reversible optical bleaching is given in terms of the band theory of solids. A model is then proposed for evanescent pink sodalite (hackmanite) which is consistent with these ideas. Optical, x-ray and chemical measurements are in qualitative agreement with this model. It is shown that the presence of sulfur (1, 2), or manganese (3) is not a necessary condition for the evanescence. This is in agreement with the observations of Walker and Parsons (4) on hackmanite from Bancroft, Ontario, and Miser and Glass (5) on hackmanite from Magnet Cove, Arkansas. Synthetic materials have been prepared which exhibit darkening under 2537 Å u.v. and subsequently bleach under visible light or heat.

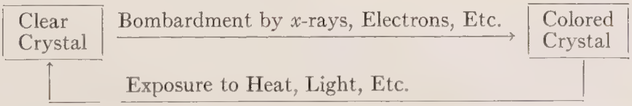
Historical Background

Our studies of hackmanite and tenebrescence originated with W. E. Bradley, Director of Research, Philco Corporation. He felt that substances which exhibited purely optical reversible bleaching (if they existed) were capable of extensive electronic applications. Dr. W. G. Gibson was asked by Mr. Bradley if he knew of any natural mineral which darkened under ultra-violet light and bleached under visible radiation. Dr. Gibson consulted the Delaware County Institute of Science (Media, Pa.) and Mr. Fox of that organization suggested the mineral, hackmanite, which was reported by O. Ivan Lee (3) to exhibit this effect.

Members of the Institute and of the Academy of Natural Sciences (Phila.) furnished a few small specimens. W. E. Bradley visited Bancroft, Ontario, and obtained more specimens with the assistance of Mr. Louis Moyd, an economic geologist of that region. It was with the latter specimens that most of our measurements were obtained.

I. Introduction

The properties of crystals which have been discolored and then bleached by various radiations constitute one of the central problems in solid-state physics. The term "tenebrescence," Latin-tenebrae (shadows), has been applied to this reversible process which may be graphically depicted as follows:


Clear Crystal
Bombardment by x-rays, Electrons, Etc.
Colored Crystal
Exposure to Heat, Light, Etc.

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A qualitative model of the phenomenon has been constructed from the results of the quantum theory of solids and the researches of Pohl and his co-workers with the F-centers (color centers) of the alkali halides (6–9). Most fundamental investigations of tenebrescence have dealt exclusively with the alkali halides, since, in addition to their relative simplicity, they were readily available in large single crystals of high optical purity (10).

The reversible discoloration of alkali halides was originally observed by E. Goldstein (11) late in the last century. The characteristic colors produced in KCl (magenta), NaCl (yellow), KI (blue), and KBr (blue-green) under electron bombardment faded upon exposure to ambient light. Later investigators observed that the discoloration could also be produced by *x*-rays, very short wave length ultra-violet, or by addition of a stoichiometric excess of the alkali metal.

In addition to the alkali halides, a large group of other materials exhibit tenebrescence. These include: the silver halides (12), the alkaline earth fluorides (13), magnesium oxide (14), titanium dioxide (15), and a great many minerals (16).

In the following discussion, our interest will be focused on the properties of a particular mineral, hackmanite, which is also known as evanescent pink sodalite. This interest in hackmanite is due to its unique property of darkening under *long* wavelength ultra-violet.

Hackmanite antedates the alkali halides in terms of the bleaching aspects of tenebrescence. In 1834, Robert Allan in his Manual of Mineralogy stated, "Its color is green unless freshly fractured, when it presents a brilliant pink tinge, but this on exposure to light goes off in a few hours." Mineralogists regarded this record as poorly founded and Allan's discovery was ignored. In 1901, the first of a series of investigations (1), (17), (4) confirmed his observations. The tenebrescence cycle was completed by Lee's discovery (3), that exposure to ultra-violet light up to about 4800 Å produced the characteristic magenta coloration which could be bleached by a bright light. Lee's investigations have yielded most of the physical information on hackmanite (as reported in the literature) and his results therefore merit some further discussion.

Hackmanite when subjected to excitation from an iron-spark discharge (2 cm. 10 sec.) showed a brilliant salmon pink fluorescence and a weak blue-white phosphorescence. The induced color faded in the dark very slowly but exposure to a 60W lamp for 30 sec. gave almost complete reversal. The respective wavelengths are:

Darkening: 2250–4800 Å
Bleaching: 4800–7500 Å

The peak efficiency of bleaching occurs at wavelengths shorter than yellow. Following reversal, there is some partial recovery of coloration if the specimen is kept in the dark for more than five weeks.

Lee's analysis of the tenebrescence phenomenon in hackmanite appears to have been dominated by the researches of Doelter (18) who thought, that color changes in minerals through ultra-violet, (u.v.) x-ray, and Ra-radiation were due to oxidation and reduction changes of metallic oxides. The work of the Göttingen group on the tenebrescence of the alkali halides had not yet found its way into English technical literature.

Although Lee's article posed some tantalizing questions, no further work was done in the directions he suggested as far as we could determine. Other reports of the evanescent pink sodalite keep cropping up in the literature and some of these are listed in (19–21).

II. THE COLOR CENTER MODEL FOR HACKMANITE AND SODALITE

The optical properties of hackmanite can be described in terms of the band theory of solids. Consider Fig. 1. Figure 1*a* is the representation of an insulator with the highest filled band and the empty conduction band shown. This may be considered as the band picture of pure sodalite. Figure 1*b* indicates that narrow bands of additional permissible energy levels may arise. Those marked F can be considered due to normal lattice imperfections such as cracks, strains, and missing ions. These constitute electron traps and upon capture of an electron are converted into F-centers. This corresponds to the situation in the alkali halides and the terminology of color centers in alkali halides will be applied to hackmanite optical phenomena. It should be considered that Fig. 1*a* represents an ideal case and that in most crystals, levels corresponding to $F(1b)$ will be found even if no chemical impurities are added. The levels at U are responsible for the sensitivity of hackmanite to ultra-violet and may be considered as arising from the introduction of a substitutional or interstitial

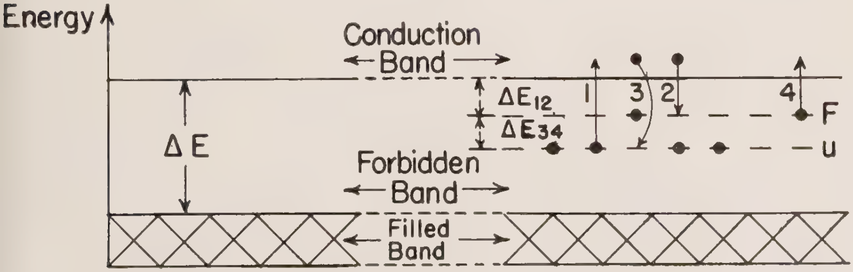


Fig. 1a. Fig. 1b.

FIG. 1

impurity into the sodalite lattice. This model makes possible the complete description of the evanescence phenomena in terms of electronic transitions.

Consider the completely bleached crystal. If it is exposed to ultraviolet (2000–3600 Å; upper limit given as 4800 Å by Lee) electrons are raised from the normally populated levels at U into the conduction band (process (1) $-h\nu = \Delta E_{12} + \Delta E_{34}$). These conduction band electrons then have the option of either being trapped at an empty F-level (2) thus forming an F-center or recombining with holes in the U levels (3), i.e., there is a strong competition between traps at F and holes at U for the conduction band electrons.

The transition (2) is assumed responsible for the bright salmon-orange fluorescence of hackmanite observed during the U. V. irradiation.

The crystal is now in the colored state since the trapped electrons at *F* constitute F-centers. If a quantum of radiation corresponding to $h\nu = \Delta E_{12}$ is incident on the crystal it may be absorbed by an F-center. The electron in the F-center is excited into the conduction band where the same (2)–(3) competing processes take place. After a sufficient time, the crystal can be considered as bleached. Thermal bleaching occurs in an analogous manner although in this case, the activation energy is lowered by the lattice vibrations. If we assume that the capture cross-section (σ) of the U-levels is of the same order of magnitude as the capture cross-section (σ) of F-levels, then we may conclude that substances showing a high degree of darkenability have a low bleaching efficiency and conversely.

In order to complete our picture we must use this model to explain the discoloration of clear hackmanite left in the dark. Assume that at absolute zero ($T = 0°K$) the U-levels are completely populated whereas the F-levels are all empty. At any other temperature there exists a finite probability of transition from the U-levels to the F-levels, and vice versa, and at this temperature there is a unique equilibrium distribution of the electrons among these levels. The temperature dependence of this equilibrium distribution may be determined from statistical considerations as:

$$n = Ae^{-\Delta E/2kT}$$

wherein n represents the number of F-centers, ΔE, a thermal activation energy which is at least less than $\Delta E_{max} = \Delta E_{34}$, A is a constant depending on the original number of empty F-levels per cm.^{3} and the original number of filled U-levels per cm^3. For hackmanite, it is found that ΔE is rather small ($\Delta E_{max} \cong 1$ ev) so that at room temperature, we should expect an appreciable number of F-centers to be formed in crystals shielded from light as is observed.

III. Optical Measurements

In order to determine the trap and activator spectrum of hackmanite which differentiates it from sodalite, an investigation of the absorption coefficient (K) was undertaken. The work was hampered by the inability to procure clear homogeneous crystals of hackmanite. Scattering effects of minute impurities in the specimens investigated were neglected. The absorption coefficient was measured using two different methods.

(*a*) *Method 1*

Measurements of K were obtained in the range of 4200 Å–6200 Å in steps of 25 Å using the apparatus setup of Fig. 2. A balancing circuit using a compensating photocell for stray radiation is not shown. The calibration and use of the spectrometer are described in the Bausch and Laumb Spectrometer Catalogue 33-82-09. The results given in Fig. 3 show the existence of an absorption band whose amplitude depends on time of exposure to the ultra-violet. The position of the maximum is invariant with the exposure time and corresponds to an F-level depth of 2.34 electron-volts (e.v.).

(*b*) *Method 2*

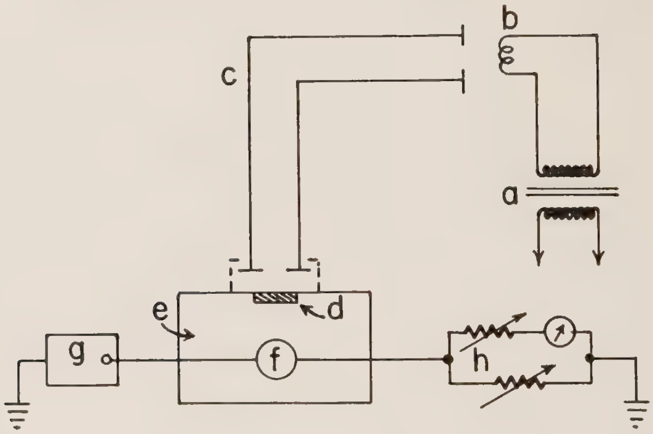
We were able to extend the range of our measurements by use of the Beckmann Model DU Spectrophotometer. I was permitted to use this instrument through the courtesy of Dr. P. H. Miller, Jr., and the Physics Department of the University of Pennsylvania. D. A. Melnick assisted in these measurements.

Readings were taken every 50 Å units in the new range of 2200 Å–18,000 Å. Much tedious calculation was avoided in using this instrument since density values can be directly obtained through the calibration of the equipment. The results are shown in Figs. 4 and 5. The shape of the absorption curve (ΔK) in Fig. 5 is of particular interest since it exhibits a unique characteristic of the F-bands in the alkali halides: a linear rise in the short wavelength region which is believed to be due to the excitation of the localized F-center electron into hydrogen like energy levels. The continuous absorption here is of the same order of magnitude as the band absorption.

The rise of the absorption coefficient in the ultra-violet is marked by a series of peaks. This effect may be due to a set of discrete activating levels instead of the narrow continuous band previously thought to be responsible for the darkening of hackmanite under U.V. As expected, *K* decreases somewhat in the U.V. region after exposure.

We can thus state the following general conclusions from our work with absorption coefficients:

1. The peak of the F-band (if we may so designate it) in hackmanite occurs at 5300 ± 50 Å which corresponds to a value of about 2.34 electron volts. We consider this as the difference in the *IS* and *2P* states of an F-center electron, but to a good approximation it represents the depth



a- Sola constant voltage transformer
b- 100 watt mazda bulb with reflector
c - Bausch and Lomb large Spectrometer
d- Ground and polished specimen of Hackmanite
e- Light tight box
f - Photomultiplier (RCA-931A)
g- Regulated power supply for Photomultiplier
h- Galvanometer System

Apparatus for measurement of Absorption Coefficient

FIG. 2

of the electron traps below the conduction band. The peak of the F-band is not dependent on the amount of prior excitation.

2. There is an auxiliary band which might be an F^1 band at 6000 Å. This could be verified by a close inspection of its temperature properties.

3. The quantum yield for hackmanite is very low when compared with substances such as KCl which have been darkened under electron bombardment. For the specimens investigated, the maximum number of color centers obtainable is $n_0 = 10^{17}/\text{cm}^3$. This number ($n_0$) may be calculated from the absorption coefficient (ΔK) by use of an expression due to Smakula (22).

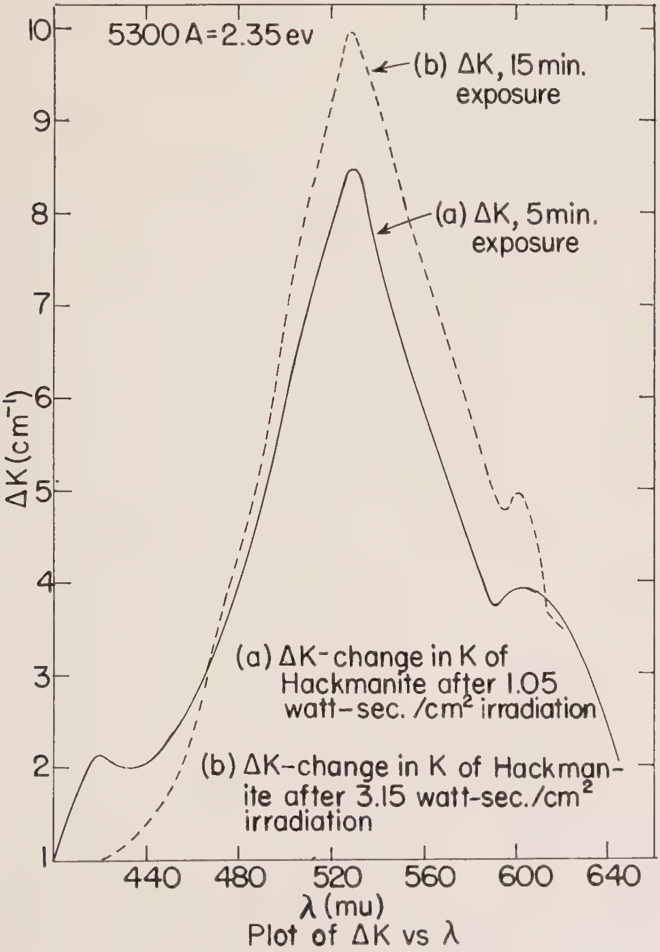
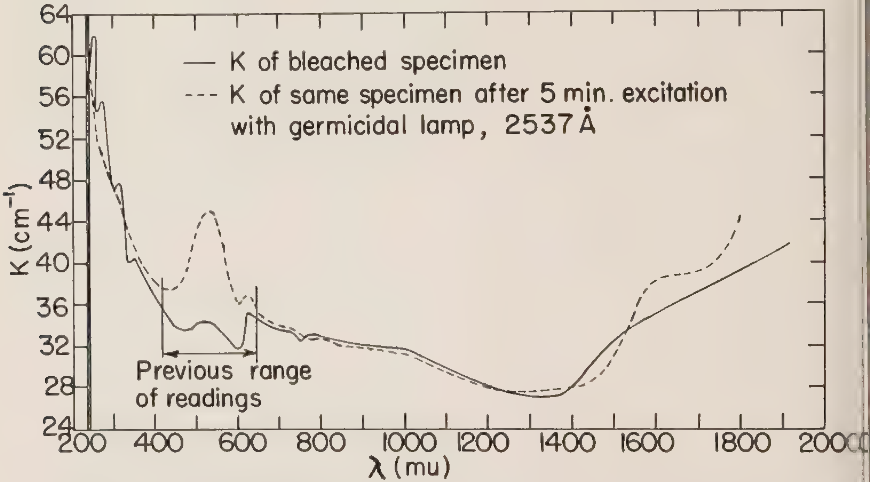


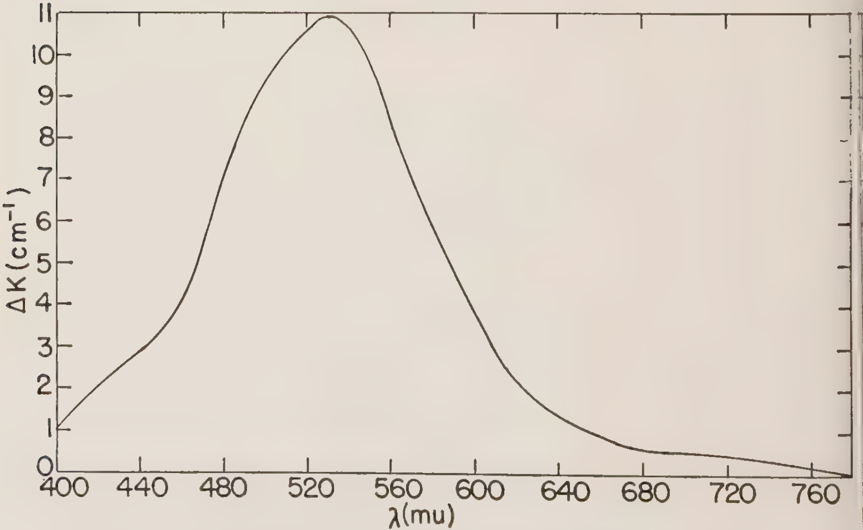
FIG. 3

4. The absorption band produced in hackmanite, protected from external radiation, is of the same general form as the F-band with its peak at 5300 ± 50 Å. There are some irregularities in it which do not occur in



Absorption coefficient (K) of Hackmanite before and after excitation with ultra-violet

Fig. 4



ΔK vs λ for Hackmanite which has been exposed for 5 min. to radiation from a 15 watt germicidal lamp (1.05 watt-sec./cm^2)

Fig. 5

TABLE 1

	Sodalite (Blue)			*Hackmanite*				
Author	Thomson	Vredenburg	Miser & Glass	Borgström	Walker & Parsons	Lee	Miser & Glass	Medved
Source	Greenland	Rajputana, India	Magnet Cove, Ark.	Kola Pen., U.S.S.R.	Bancroft, Ont.		Magnet Cove, Ark.	Bancroft, Ont.
Comp %								
SiO_2	38.52	38.055	38.36	36.99	37.08	—	36.70	—
Al_2O_3	27.48	31.300	32.09	31.77	32.58	—	32.01	—
Na_2O	23.50	24.77	24.73	25.84	22.26	—	24.79	—
Cl	3.0	7.18	6.79	6.44	6.82	—	7.00	—
Fe_2O_3	—	trace	0.07	0.17	—	—	0.07	.00x
FeO	—	—	none	—	—	—	none	
TiO_2	—	—	none	—	—	—	none	none
MnO	—	—	0.06	—	trace	.0015	none	.000x
MgO	—	—	none	none	0.03	—	none	none
K_2O	—	—	0.12	0.16	0.53	—	0.17	1.0–5.0
CaO	—	0.001	0.5	—	—	—	0.29	1.0–5.0
CO_2	—	—		—	0.32	—		—
Li	—	—	—	—	—	.01	—	—
Ga	—	—	—	—	—	.01	—	.00x
Pb	—	—	—	—	—	.005	—	none
Be	—	—	—	—	—	trace	—	none
Ba	—	—	—	—	—	trace	—	none
Sr	—	—	—	—	—	trace	—	.00x
Nd	—	—	—	—	—	1 line @4303	—	—
S	—	—	none	0.39	none	—	trace	none
SO_3	2.10	trace	trace	—	—	—	trace	none
P				—	—	trace	—	—
H_2O	1.70	0.82	0.86	—	0.67	—	0.36	0.24–0.35

the band produced under U.V. and these were not always reproducible. The temperature variation of the intensity produced over a given length of time should give us conclusive evidence as to the validity of our hypothesis concerning this phase of darkening.

IV. CHEMICAL CONSIDERATIONS

Table 1 is a summary of the available information on the chemical composition of hackmanite and sodalite. From a comparison of the various analyses we made the following tenative conclusion:

(*a*) The amount of SiO_2 in hackmanite is less than that in sodalite by $\simeq 1\%$.
(*b*) The data on manganese is conflicting.
(*c*) The data on sulfur is conflicting.
(*d*) There is less water in hackmanite than in sodalite.

Since manganese and sulfur are important elements in phosphor synthesis, we were particularly interested in the dependence of the tenebrescent properties of hackmanite on the relative amounts of these elements.

Dana (2) claims that hackmanite is sodalite containing 6.23% of Na_2S, i.e., it is a mixture of sodalite and lapis-lazuli (lazulite). He does not give the source of his information but since he lists the Kola Peninsula (USSR) as the site of occurrence, we concluded that his information came from the paper by Borgström (1). However, no $S^=$ or $SO_3^=$ was found in the hackmanite specimens we investigated. These were from Bancroft, Ontario. (We have prepared a synthetic material whose properties resemble those of hackmanite and which is essentially pure sodalite which has been heated in a reducing atmosphere with no sulfur present—see below.)

The synthesis of sodalite was carried out using the work of the BPI group as its basis (23). Where the BPI group used Na_2CO_3 we used NaOH i.e.

$$6\,NaOH + 3\,Al_2O_3 + 6\,SiO_2 + 2\,NaCl \rightarrow \qquad (1)$$
$$Na_6Al_6Si_6O_{24}\cdot 2\,NaCl + 3\,H_2O$$

A stoichiometric mixture of Al_2O_3, SiO_2, NaOH and NaCl according to eq. 1 was thoroughly mixed in a porcelain mortar and subsequently ball-milled. The resulting powder was tightly packed into a covered platinum crucible, immersed in a sand bath and placed into the cold oven. The temperature was then slowly raised to 1060° C. where it remained for a 24–72 hour period. Crystal growth at this temperature occurs pyrolytically, i.e., we are below the melting point of sodalite (which is about 1100°) and the formation of sodalite occurs through the medium of solid state reactions. If the temperature was permitted to exceed 1060° C. by any appreciable amount, sodalite was not formed. Instead, an opaque glass was obtained giving a diffuse diffraction pattern and a tan coloration under *x*-rays. The formation of this glass may be considered as analogous to the transformation of a nepheline melt into carnegieite if appropriate mineralizers are not present (24). Crystallization from the melt was therefore not accomplished. Attempts to grow larger crystals by means of mineralizers (LiF, $NaWO_4$, etc.) were not successful. Powder patterns identified the product as pure sodalite. This sodalite darkened under *x*-rays to give the characteristic magenta coloration. Measurements showed that the induced absorption band peaked at 5300 Å. This constituted a strong verification of the color center hypothesis, since the traps responsible for the F-band in hackmanite are proven to be unique to the sodalite lattice. They cannot owe their origin to the presence of extraneous impurities since this coloration was induced in pure sodalite. The x-rays provided sufficiently energetic photons (ΔE) so that the excited electrons could bridge the forbidden gap between the conduction band and the filled band (see Fig. 1*a*).

In connection with the absorption bands produced by x-rays in the sodalite-hackmanite system some interesting facts came to light concerning the natural minerals. The following sequence of events was observed.

For Natural Sodalite

$$\text{Blue} \xrightarrow[\text{450° C.}]{\text{(heat)}} \text{Colorless} \xrightarrow{(x\text{-rays})} \text{Blue, etc.}$$

For Natural Hackmanite

$$\text{Colorless} \xrightarrow{\text{(U.V.)}} \text{Magenta} \xrightarrow[\text{250° C.}]{\text{(heat)}} \text{Colorless} \xrightarrow{\text{(U.V.)}}$$

$$\text{Colorless} \xrightarrow{(x\text{-rays})} \text{Blue} \xrightarrow[\text{up to 600° C.}]{\text{(heat)}} \text{Colorless} \xrightarrow{(x\text{-rays})} \text{Blue, etc.}$$

The color changes of blue sodalite to colorless and of hackmanite irreversibly bleached by heat were accompanied by weight losses. Hackmanite and sodalite samples were weighed before and after heat treatment. The results are shown in Table 2.

TABLE 2

Hackmanite			*Sodalite*		
Temp. ° C.	% Wt. Loss	Loss of U. V. Sen.	Temp.	% Wt. Loss	Loss of Color
1000	1.26	yes	600° C.	1.37	yes
800	0.72	yes	500° C.	1.42	yes
500	0.35	yes	550° C.	1.28	yes
200	0.056	no			

During these experiments it was found that the surface of hackmanite changes in appearance from a crystalline translucent material to chalk white. Part, but not all of the loss, was shown to be water. It is of interest to note that:

1. The heat treatment serves to shift the position of the F-band to longer wavelengths

in addition to driving off the activating impurities in hackmanite which give rise to the U-levels.

2. Sodalite which is heated above 450° C. and not exposed to radiation such as x-rays is colorless. It might prove fruitful to investigate specimens of colorless and blue sodalite as found in the natural state and to correlate this difference in terms of temperature histories.

The temperature scheme for the artificial substances is as follows:

For Synthetic Sodalite

$$\text{Colorless} \xrightarrow{\text{(U.V.)}} \text{Colorless} \xrightarrow{(x\text{-rays})} \text{Magenta} \xrightarrow[700^\circ]{\text{(heat up to)}}$$

$$\text{Colorless} \xrightarrow{(x\text{-rays})} \text{Magenta, etc.}$$

For Synthetic "Hackmanite"

$$\text{Colorless} \xrightarrow{\text{(U.V.)}} \text{Magenta} \xrightarrow[700^\circ]{\text{(Heat up to)}} \text{Colorless} \xrightarrow{\text{(U.V.)}} \text{Magenta, etc.}$$

The irreversible loss in sensitivity to U.V. of natural hackmanite and the concomitant loss in mass upon heating may be due to a loss of the activating compounds which produce the U.V. sensitive centers. The shift in the F-band of natural hackmanite under heating and the discrepancies between the behavior of the natural sodalite-hackmanite system and the artificial sodalite-hackmanite system indicate that we have not duplicated the natural substances exactly.

We found that the substitution or addition of the following elements in varying amounts did not introduce the necessary U-levels into pure sodalite.

Sm, Cu, Ti, Ni, Mg, Ca, Cd, Mn, Pb,
Sn, Mo, Zn, Y, Cs, Ce, Ba, Ge, La,
Sr, Ag, Bi, Hg, Co, S

Firing the pure sodalite in atmospheres of nitrogen, air, oxygen, steam, and CO_2 also gave no additional levels although darkening was still possible with x-rays.

However, if the sodalite were fired in a reducing atmosphere of hydrogen or in a carbon crucible with limited access to the atmosphere, the specimens became strongly sensitized to 2537 Å U.V., i.e., the required U-levels appeared. However, although natural hackmanite shows a fair response to 3600 Å U.V., the synthetic form had only weak sensitivity at this wavelength. The characteristic salmon-orange fluorescence was also observed although somewhat weaker than in the natural substance.

It seems very tempting to identify these U-levels and the corresponding absorption band, with the U-bands observed by Hilsch and Pohl in

KBr which has had some of the Br^- lattice sites replaced by H^- (25). The electronic transition can be considered as one in which an electron is raised from the H^- into a state extending over the neighboring metal ions. This condition is similar to the excited state of a halogen ion in the pure crystal which gives rise to the intrinsic absorption band. However, the formation of the F-band is not clearly understood. Mott and Gurney (26) believe it forms when the excited electron leaves a hydrogen atom behind which diffuses away at room temperature. The electron then falls back into the vacated lattice site and forms an F-center. However, this theory when applied to hackmanite has its shortcomings.

In our investigations, we have implicitly assumed that the basic $(NaAlSiO_4)_6$ lattice of sodalite is relatively stable and optically inert. Thus, it is in the $\cdot 2NaCl$ part that we seek our explanations. If Cl^- is replaced by H^- then $NaCl => NaH$ is analogous to $KBr => KH$. However, the present theory of U-center transformation to F-centers is unsatisfactory if we consider the activating reaction as being $\cdot NaCl \rightarrow \cdot NaC$, when we consider the more immobile carbon atom.

We have used the band theory of color centers to help elucidate the peculiar properties of hackmanite. On the other hand, further investigations of the hackmanite-sodalite materials may prove of importance in our basic ideas of color centers.

V. SUMMARY

The unique optical properties of hackmanite have been explained in a phenomenological manner, utilizing the present role of color centers in the band theory of solids. We have found that pure bleached sodalite will darken to a magenta coloration only under x-rays. The darkening is considered to take place in two stages, (1) Electrons are promoted from the filled band to the conduction band by the highly energetic x-ray photons, and (2) These conduction band electrons are trapped at negative ion vacancies (in this case considered to be Cl^-) forming F-centers. Absorption measurements give 2.34 electron volts as the F-level depth. When exposed to visible light, the specimen appears colored since quanta corresponding to this energy are being absorbed. The process is analogous to writing with a pencil on a sheet of white paper; light is absorbed at the graphite trace. The color is observed to fade under a bright light since the F-centers are eventually emptied. This represents erasure or bleaching.

Hackmanite darkens to the same magenta coloration, but only long wavelength ultra-violet is needed. Thus, some type of electron donor levels arising from a substitutional or interstitial impurity in sodalite are needed. The existence of these donor levels lowers the energy required to excite electrons into the conduction band. This is stage (1) which can be carried out with 2537 Å or 3600 Å quanta. Stage (2) proceeds as before and the specimen has thus been darkened with ultra-violet. The absorption maximum is also at 5300 ± 50 Å (about 2.34 e.v.).

In synthetic hackmanite which was prepared by heating sodalite in a reducing atmosphere, we can identify these donor levels as U-centers. A U-center is formed in KBr when a Br^- ion is replaced by a hydride ion, H^-. If the Mott-Gurney mechanism for the U-center to F-center transformation is correct, then the following hypothesis can be applied to formation-transformation of a generalized U-center.

(1) A U-center is formed whenever an ion is substituted for the normal lattice negative ion, the substituted ion having a considerably lower electron affinity than the lattice ion (cf. hydride or carbide ion with chloride ion electron affinity).

(2) The transformation to an F-center only occurs when the substituted ion (H^- or C^-) has a small ionic radius and a low mass number so that atomic diffusion through the lattice is facilitated.

Acknowledgment

I wish to thank Mr. W. E. Bradley for his continuing guidance and stimulation through every phase of this work. I am indebted to Mr. H. A. Affel, Jr., for his patience, forebearance, and help in his capacity as project engineer with a study whose electronic potentialities were not always evident, to Mr. R. E. Waggener for his fruitful discussions and suggestions, and to Miss Sally Kerr for her able technical assistance.

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CALLAGHANITE, A NEW MINERAL

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ABSTRACT

Studies of small, azure-blue crystals from the working pits of the Gabbs Refractories, Inc., Gabbs, Nevada lead to the description of a new hydrated basic copper, magnesium, calcium carbonate, $Cu_4Mg_4Ca(OH)_{14}(CO_3)_2 \cdot 2H_2O$. The mineral is named callaghanite after Dr. Eugene Callaghan, Director, New Mexico Bureau of Mines and Minerals, in recognition of his geological work on magnesite deposits. The mineral occurs near peridotite dikes intrusive into magnesite and dolomite.

Cleavages are $\{111\}$ and $\{\bar{1}11\}$, perfect; brittle; hardness is 3–3½; transparent; habit, pyramidal. Calculated specific gravity is 2.78; measured, 2.71.

X-ray studies by Weissenberg and precession methods show callaghanite to be monoclinic; space group either $C_s^4—Aa$ or $C_{2h}^6—A2/a$; and cell dimensions $a_0 = 8.24\text{Å}$, $b_0 = 11.80\text{Å}$, $c_0 = 10.06\text{Å}$, $\beta = 107°18'$. Elements calculated from *x*-ray data are: $a:b:c = 0.6983:1:0.8525$; $p_0:q_0:r_0 = 1.2209:0.8140:1$; $\mu = 72°42'$; $p_0' = 1.2788$, $q_0' = 0.8525$, $x_0' = 0.3115$. The unit cell contains $Cu_8Mg_8Ca_2(OH)_{28}(CO_3)_4 \cdot 4H_2O$.

Crystal forms present are $\{111\}$, $\{111\}$, $\{221\}$, and $\{\bar{2}21\}$. Elements calculated from the goniometric data are: $a:b:c = 0.7252:1:0.8504$; $p_0:q_0:r_0 = 1.2168:0.8092:1$; $\mu = 72°5'$ $p_0' = 1.2788$, $q_0' = 0.8504$, $x_0' = 0.3094$.

Optical data are: $\alpha = 1.559$, $\beta = 1.653$, $\gamma = 1.680$; $2V = 55°$; optically $(-)$; $Z \wedge c = 18°$; pleochroic in blue with absorption $Z > Y > X$; $r > v$, strong.

INTRODUCTION

In the summer of 1952 while the senior writer was doing field geology in Nevada, Mr. Conrad Martin, consulting geologist, Reno, Nevada, called his attention to the occurrence of small azure-blue crystals disseminated through magnesite and dolomite beds near Gabbs, Nevada (Fig. 1). Mr. Martin had noted that the crystals effervesced slowly in dilute HCl and gave qualitative tests for copper and magnesium. With the permission of Basic Refractories, Inc., Gabbs, Nevada, a collection of the blue crystals was made and brought back to the laboratory for identification.

Mr. Martin has supplied most of the following information on the occurrence of this new mineral. The rocks along the west flank of the Paradise Range in the vicinity of Gabbs, Nevada are carbonates of an undetermined thickness. These carbonate rocks are part of the Luning formation of Upper Triassic age, and consist dominantly of dolomite with substantial masses of crystalline magnesite. In the vicinity of Gabbs the carbonate rocks are intruded by diorite and quartz diorite rocks. At the contact between magnesite and diorite, magnesite has been changed to brucite and diorite has become more basic by assimilation of magnesia.

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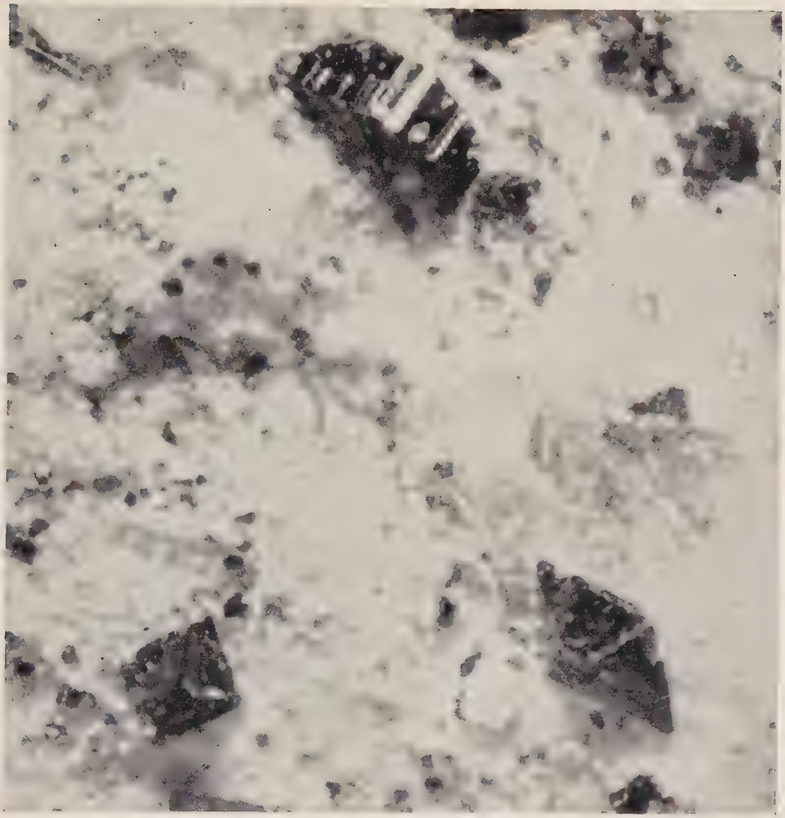

FIG. 1. Callaghanite crystals on dolomite rock. ×34.

Apophyses of diorite within brucite may be changed completely to serpentine. A thin band of forsterite often marks the boundary between the serpentine and brucite. The new mineral generally is found within this serpentine-forsterite-brucite zone where it occurs as tiny disseminated crystals (Fig. 1), as encrustations (Fig. 2), and as veinlets. The field relationship of the mineral suggests that it is hydrothermal in origin. From the chemical composition (below) the writers suggest that the ore-forming solution would normally have precipitated azurite but, in the presence of magnesium and calcium from the surrounding sedimentary rocks, formed a new mineral.

When the mineral could not be identified from a powder x-ray picture, a more complete study was made. The writers are indebted to Professor J. Waser, Department of Chemistry, Rice Institute, Houston, Texas, for permission to use his Weissenberg and precession cameras for the single crystal results reported herein, and to Professor S. E. Clabaugh, Department of Geology, University of Texas, Austin, Texas, for the use of a two-circle goniometer.

The new mineral has been named *callaghanite* after Dr. Eugene Callaghan, Director, New Mexico Bureau of Mines and Minerals, Socorro, New Mexico, in recognition of his geological work on magnesite deposits including the Gabbs deposit in which the mineral was found.

PHYSICAL PROPERTIES

The specific gravity of callaghanite was determined by two methods: (1) by means of a microchemical analytical balance, on which the crystals were first weighed in air and then in a mixture of bromoform and n-amyl alcohol with a specific gravity of 1.915; and (2) by suspension in a heavy liquid mixture of bromoform and acetone. These procedures were necessitated by the small size of the crystals, which range from microscopic up to 1.5 mm. in length, and by the fact that the total amount of material for study was small. Three crystals, aggregating 6.06 mg., were used. A specific gravity of 2.71 was obtained by both methods, a reasonable check with the theoretical value of 2.78 (below).

The cleavages of callaghanite are perfect parallel to the unit positive fourth-order prism, $\{111\}$, and unit negative fourth-order prism, $\{\bar{1}11\}$. Hardness is $3\text{–}3\frac{1}{2}$; luster, vitreous; fracture, irregular; color, azure-blue; streak, white; diaphaneity, transparent; tenacity, brittle.

STRUCTURAL CRYSTALLOGRAPHY

The tiny crystals of callaghanite were admirably suited for single crystal studies. Rotation, Weissenberg, and precession pictures were taken using CuK_α radiation. The Weissenberg and precession pictures indicated monoclinic symmetry, and the extinctions were characteristic of either the space group C_s^4-Aa or the space group C_{2h}^6-A2/a. An experiment to determine pyroelectricity gave negative results; therefore, it is not known whether callaghanite is centrosymmetrical or not. The cell dimensions are: $a_0=8.24\pm.03$ Å, $b_0=11.80\pm.03$ Å, $c_0=10.06\pm.04$ Å, $\beta=107°18'\pm30'$. Elements calculated from x-ray data are: $a:b:c=0.6983:1:0.8525$; $p_0:q_0:r_0=1.2209:0.8140:1$; $\mu=72°42'$; $p_0'=1.2788$, $q_0'=0.8525$, $x_0'=0.3115$.

X-RAY POWDER PATTERN

The x-ray powder pattern of callaghanite is shown in Fig. 3. The estimated intensities and the measured θ and d values are given in Table 1. The pattern has been indexed as far as $\theta=27.17°$, and the measured values agree with one or more theoretical values.

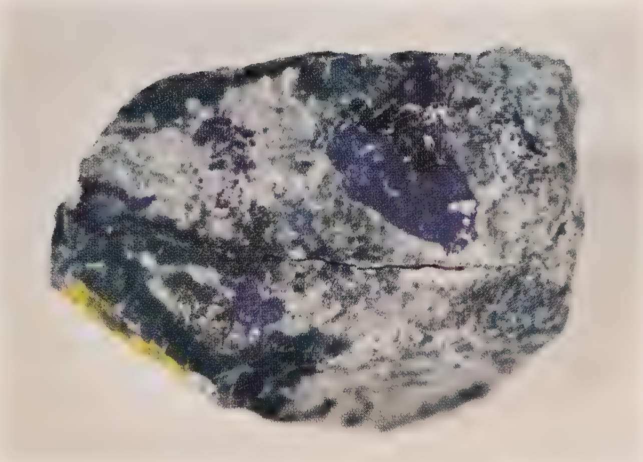

FIG. 2. Encrustation of callaghanite on serpentine rock. ×2.

TABLE 1. CALLAGHANITE: X-RAY POWDER PATTERN

Monoclinic, C_s^4—Aa or C_{2h}^6—$A2/a$; $a_0=8.24$ Å, $b_0=11.80$ Å, $c_0=10.06$ Å, $\beta=107°18'$

I	θ (Cu)	*d* (meas.)	(*hkl*)	*d* (calc.)	*I*	θ (Cu)	*d* (meas.)	(*hkl*)	*d* (calc.)
10	5.95°	7.45 Å	(011)	7.45 Å	2	20.32°	2.22 Å	$(\bar{2}24)$	2.21 Å
10	7.17	6.17	$(\bar{1}11)$	6.17	1	20.92	2.16	(151)	2.16
6	9.25	4.80	(002)	4.80	2	22.10	2.05	(313)	2.05
9	11.50	3.87	(200)	3.93				$(\bar{3}33)$	2.05
6	11.95	3.72	(022)	3.72				(402)	2.05
9	14.02	3.18	$(\bar{2}22)$	3.08				$(\bar{2}51)$	2.04
			$(\bar{1}13)$	3.20	2	23.15	1.96	(400)	1.96
2	15.12	2.95	(040)	2.95				(340)	1.96
2	16.20	2.76	(140)	2.76				(060)	1.97
			(041)	2.76	1	23.45	1.94	(224)	1.95
			(113)	2.74	1	23.72	1.91	(160)	1.91
6	16.75	2.67	$(\bar{3}11)$	2.67				(251)	1.92
2	17.65	2.54	(231)	2.53	1	24.47	1.86	(044)	1.86
			$(\bar{1}42)$	2.51				(420)	1.86
			(042)	2.51	5	25.20	1.81	$(\bar{1}62)$	1.81
			(033)	2.48				(062)	1.82
4	18.75	2.40	(004)	2.40				(204)	1.82
			(320)	2.42	2	26.00	1.76	(115)	1.76
			$(\bar{2}04)$	2.39				$(\bar{2}15)$	1.76
4	19.02	2.36	(240)	2.36				(053)	1.75
7	19.55	2.30	(051)	2.29	2	26.50	1.73	(162)	1.73
			(142)	2.29				$(\bar{2}62)$	1.73
2	20.32	2.22	(024)	2.23	1	27.17	1.69	(026)	1.67

I	θ (Cu)	*d* (meas.)	*I*	θ (Cu)	*d* (meas.)	*I*	θ (Cu)	*d* (meas.)
1	27.72	1.66	½	32.85	1.42	2	39.00	1.23
4	28.80	1.60	½	33.15	1.41	3	39.50	1.21
1	29.20	1.58	2	33.90	1.38	2	40.70	1.18
1	29.90	1.55	2	34.97	1.34	½	40.90	1.18
2	30.45	1.52	1	35.35	1.33	2	41.80	1.16
2	30.80	1.51	½	35.80	1.32	½	42.30	1.15
1	31.55	1.47	2	36.65	1.29	1	43.35	1.12
2	32.17	1.45	2	37.45	1.27	½	43.85	1.11
5	32.42	1.44	2	37.75	1.26	½	44.65	1.10

MORPHOLOGICAL CRYSTALLOGRAPHY

Five separate crystals of callaghanite were used for the measurement of interfacial angles on a two-circle goniometer. Three of these crystals were mounted with the *c*-axis parallel to the axis of the goniometer head; two with the *b*-axis parallel to the axis of the goniometer head. Four of the crystals showed only $\{111\}$ and $\{\bar{1}11\}$ forms, equally developed, but

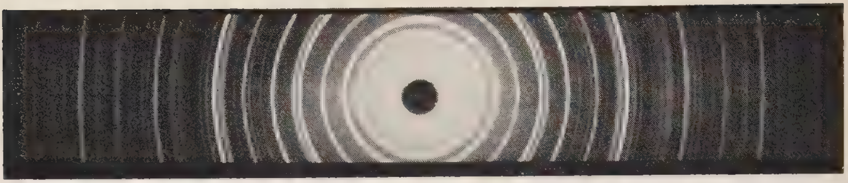

FIG. 3. X-ray powder pattern of callaghanite.

the other crystal showed not only {111} and {$\bar{1}$11} forms but also {221} and {$\bar{2}$21} forms. Hand lens inspection of twenty other crystals showed no development of either {221} or {$\bar{2}$21}. The faces were megascopically excellent, but gave fair to poor reflections. Figure 4 illustrates an idealized crystal of callaghanite drawn from goniometric data. Table 2 summarizes the goniometric data. The average of the measured angles agrees closely with the calculated angles. Elements calculated from goniometric data are: $a:b:c=0.7252:1:0.8504$; $\beta=107°55'$; $p_0:q_0:r_0=1.2168:0.8092:1$; $\mu=72°5'$; $r_2:p_2:q_2=1.2358:1.5038:1$; $p_0'=1.2788$, $q_0'=0.8504$, $x_0'=0.3094$. The elements calculated from the goniometric measurements are in agreement with the elements calculated from the x-ray data.

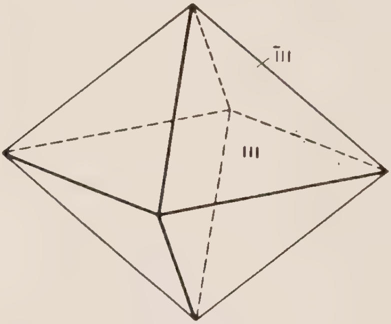

FIG. 4. Callaghanite, clinographic projection showing the forms {111} and {$\bar{1}$11}.

TABLE 2. CALLAGHANITE: CRYSTAL MEASUREMENTS, FIVE CRYSTALS—MONOCLINIC

Form	Number of Faces	Quality	Average Measured		Range		Calculated	
			Phi	Rho	Phi	Rho	Phi	Rho
{111}	10	Fair to poor	61°50′	60°58′	61°33′–61°58′	60°46′–61°07′	61°48′	61°00′
{$\bar{1}$11}	9	Fair to poor	48 46	52 12	48 39 –48 53	52 05 –52 15	48 46	52 12
{221}	2	Fair	55 26	70 23	55 14 –55 38	70 12 –70 34	55 27	70 24
{$\bar{2}$21}	2	Fair	45 12	63 15	44 58 –45 26	63 06 –63 15	45 10	63 13

Composition and Cell Content

A microchemical analysis of callaghanite is given in Table 3. Carbon dioxide and water were determined by igniting 10 mg. of sample and selectively absorbing the two constituents. CuO, MgO, and CaO were determined by fusing 25 mg. of sample with an acid flux. Copper was plated out on platinum electrodes. The remainder of the fusion product consisted of MgO and CaO, and the ratio of these constituents was determined spectrochemically. This chemical analysis gives the empirical formula, $Cu_4Mg_4Ca(OH)_{24}(CO_3)_2 \cdot 2H_2O$. The main discrepancy between the analysis and the empirical formula is that the former is slightly low in CuO and slightly high in combined MgO and CaO. The microchemical analysis combined with the cell dimensions (Table 1) and the measured specific gravity (2.71) gives the number of molecules in the unit cell, namely, two. From this the probable structural formula for callaghanite is written:

$$Cu_8Mg_8Ca_2(OH)_{28}(CO_3)_4 \cdot 4\ H_2O = 2[Cu_4Mg_4Ca(OH)_{14}(CO_3)_2 \cdot 2\ H_2O].$$

The calculated specific gravity for this structural formula is 2.78.

Table 3. Callaghanite: Composition and Cell Content

Constituent	Per Cent	Molecular Proportion	Molecular Ratio	Empirical Formula	Ideal Cell Content
CuO	38.27	.4811	3.70=4	$Cu_4Mg_4Ca(OH)_{14}(CO_3)_2 \cdot 2H_2O$	2
MgO	20.86	.5174	3.98=4		
CaO	8.89	.1585	1.22=1		
H_2O	20.51	1.1395	8.76=9		
CO_2	11.46	.2604	2.00=2		
	99.99				

Clark Microanalytical Laboratory, analyst.
104½ West Main St., Urbana, Illinois.

Optical Properties

The optical properties of callaghanite, as determined by the immersion method, are: $\alpha = 1.559$, $\beta = 1.653$, $\gamma = 1.680$; $2V = 55°$; optically (−); $Z \wedge c = 18°$; pleochroic in blue with absorption $Z > Y > X$; $r > v$, strong.

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TWINNING IN CORDIERITE

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ABSTRACT

The various possible types and patterns of twinning in cordierite are discussed, based partly on a study of cordierites from seven different Indian localities. The simple, polysynthetic (parallel and interpenetrating), and cyclic (radial, stellate and concentric) twins are distinguished and their interrelationship discussed.

Twinning is exclusively confined to the (110) and (130) faces, the former being much more common and important. Polysynthetic twinning appears to be the most common type in coarse grained rocks but large scale interpenetration of lamellae is rare. Lamellae twinned on similar planes are either parallel or make angles of 60° whereas lamellae twinned on unlike faces are inclined to each other at angles of 30° or 90°. The various possible features in interpenetrating lamellae and the nature of curved and irregular composition planes are also explained. Simple and quick methods of determining the identity of the twin planes are outlined.

It is suggested that complex twin patterns (stellate, concentric etc.) are generally confined to cordierites formed at high temperatures whereas simpler types are characteristic of cordierites formed at lower temperatures.

INTRODUCTION

Polysynthetic and cyclic or sector twinning in cordierite has been known for a long time and it has also been recognized that (110) and (130) form the most important twin planes. Lasaulx (1884), Hussak (1883), Eskola (1914), and Dittler and Kohler (1938) are among those who have referred to twinning in cordierite in some detail; but descriptions of the different types of twinning and the identity of the twin planes are not common in contemporary petrographic literature in English. An attempt is made in this paper to present a morphological study of the different types of twinning in cordierite and their inter-relationship.

Cordierite crystallizes in the orthorhombic system, and the axial elements given by Dana (1914) are: 0.5871:1:0.5585, which give the interfacial angles *mm'''* i.e. $(110)\wedge(1\bar{1}0)$ as 60°50′ and *dd'* i.e. $(130)\wedge(\bar{1}30)$ as 59°10′. These interfacial angles approximate 60° which explains the pseudohexagonal twinning in cordierite. The axes of optic elasticity, X, Y and Z coincide respectively with the crystallographic axes *c*, *a* and *b*. All the angles between the twin planes and the Y and Z directions are 30° or 60°.

MATERIAL

Cordierite-bearing rocks from fourteen widely separated Indian localities were examined. Specimens from seven localities had cordierite showing little or no twinning and the material from the other seven localities was studied in some detail. Several thin sections were cut from each of the specimens available and studied with the help of the Universal stage. Nearly all the twinned grains in each section and not less than a hundred grains per specimen were examined.

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[*] Published with the permission of the Director, Geological Survey of India.

Details of the material studied are given in Table 1:

TABLE 1

No.	Name of rock	Locality	No. of specimens examined	2V of Cordierite	Descriptive notes
1	Cordierite rock	Kiranur, Trichinopoly, Madras	Several	(−) 62°–82°	Cordierite is coarse grained, anhedral and non-pleochroic in thin sections. Inclusions of sillimanite and zircon noticed; pinitization limited.
2	Hypersthene-biotite-sillimanite-cordierite rock	Paderu, Vizag, Madras	2	(+) 64°–82°	Coarse anhedral grains of cordierite showing feeble dichroism; swarms of pleochroic haloes present; pinitization advanced. See Walker and Collins (1907).
3	Hypersthene-garnet-cordierite-biotite rock	Polavaram, West Godavari, Madras	1	(−) 78°–85°	Sillimanite and spinel also present; kelyphitic borders round spinel and intergrowths of codierite with hypersthene and quartz often seen.
4	Hypersthene-biotite-cordierite rock	Ganguvarpatti, Madura, Madras	2	(+) & (−) 60°–84°	Cordierite sometimes weakly pleochroic, pinitized along borders; positive and negative grains in the same section noticed.
5	Cordierite gneiss	Tadenpatti, Ramnad, Madras	5	(+) 68°–86°	Quartz, plagioclase, biotite, hypersthene and garnet also present. Cordierite is feebly pleochroic; pinitization very negligible.
6	Cordierite-garnet-biotite-sillimanite rock	Kadamballi, Bangalore, Mysore	1	(+) 72°–82°	Abundant pleochroic haloes, moderate pinitization and no recognizable pleochroism.
7	Enstatite-cordierite vitrophyre and cordierite-labradorite vitrophyre	Gobindpur, Bokaro coalfield, Bihar	3	(−) 68°–75°	Octahedra of magnetite abundant. Euhedral and subhedral grains of cordierite show complicated twinning. Sometimes strongly pleochroic. See Fermor (1924) and Venkatesh (1952).

CLASSIFICATION AND DESCRIPTION OF TWINNING

Twinning is exclusively confined to the (110) and (130) planes. The twinning and composition planes are identical as the twin axis can be considered to lie normal to the composition plane and hence both the terms are used synonymously. The various possible twin patterns could be classified as shown below:—

- (1) Simple (110) or (130)
  - Polysynthetic or lamellar
    - (2) Parallel lamellae
    - Interpenetrating lamellae; inclined to one another
      - at
        - (3) 30° twinned on both (110) and (130)
        - (4) 60° Twinned on either (110) or (130) only
        - (5) 90° Twinned on both (110) and (130)
  - Cyclic or Sector
    - Radial
      - (6) Trilling
      - (7) Sixling
      - (8) Twelve-sector twin ("twelveling")
    - Stellate
      - (9) Six-pointed star
      - (10) Twelve-pointed star
    - Concentric
      - (11) Triangular
      - (12) Hexagonal:
        - (*a*) parallel
        - (*b*) with 30° tilt
      - (13) Six-pointed star:
        - (*a*) pointing to corners
        - (*b*) pointing to the sides
      - (14) Twelve-sided or "dodecagonal"
      - (15) Twelve-pointed star

The twin types Nos. 9, 11, 13, 14 and 15 have not been observed during this study and do not seem to have been described in the literature. A short description of these various twin types is given below:

(1) *Simple twinning:* The crystal is made up of two individuals separated by a single composition plane. Twinning could be either on the (110) or (130) plane. The vibration directions Y and Z make angles of 60° and 30° respectively, with the trace of the (110) composition plane in a basal section, and 30° and 60°, respectively with the trace of a (130) composition plane. The X vibration direction or the *c* crystal axis coincides in both individuals and lies parallel to the line of intersection of the (110) and (130) planes. Hence, only the positions of two vibration directions, viz. Y and Z need be established. The twin axis which is per-

pendicular to the *c* axis lies very nearly in the (110) plane if it is twinned on (130) and *vice versa.*

Simple twinning is seen in all the rocks except No. 7, but simple twins with (130) as the composition plane are exceedingly rare. The simple twins are, however, scarce as compared to polysynthetic twins and tend to occur where untwinned grains are abundant.

Repetition and modification of this simple type give rise to the following other types.

(2) *Polysynthetic or multiple twinning:* The twinning here is repeated at close intervals giving rise to two sets of lamellae as typified by plagioclase felspars. The following two subclasses are easily recognized under this: (*a*) When the twin planes are all parallel to one another, it can be called "parallel repetition" (*b*) When the twin planes form two or more parallel sets inclined to one another, it can be described as interpenetration or interdigitation twinning (Figs. 2 & 3). The twin lamellae may intercept one another at angles of 30°, 60° or 90°.

When two sets of inclined lamellae intersect at 60°, the normal to the composition plane of each set of lamellae would coincide with the Z vibration direction of the other set of lamellae if both are twinned on (110) (Fig. 5), and with Y direction if both are twinned on (130). If the twinning is on both (110) and (130) and the angle of intersection is 30°, the normals to the (110) and (130) would coincide with Z and Y respectively, of the other set of intersecting lamellae.

Polysynthetic twinning producing either parallel or interdigitated lamellae is the most common type of twinning among the rocks studied. It is particularly well developed in specimens 2, 3, 4 and 5. Parallel lamellae are much more common than the prominently interdigitated type.

(3) *Cyclic or sector twinning:* The composition planes in this type of pseudohexagonal twinning radiate from a central point at intervals of 30°, 60° or 120°. Three different classes of twin patterns are recognizable under this.

(*a*) Radial twinning: In the simplest case where there are only three twin planes making mutual angles of 120°, trillings are formed; six twin planes radiating from the centre at 60° to one another result in a sixling (Rosenbusch, 1905. Figs. 53 to 55). The twin planes could possibly be either (110) or (130) but only the former has been observed. Both these are produced by like twin planes and not by a combination of unlike twin planes. The basal section of the sixling would show the Y vibration direction to be radial if twinned on (130) or Z direction radial if twinned on (110). In the case of a trilling the above relations would be reversed.

In another modification there are twelve sectors ("twelveling"), four of

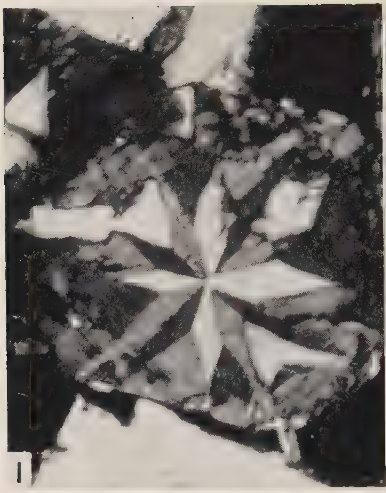

FIG. 1. Stellate twin. ×100.

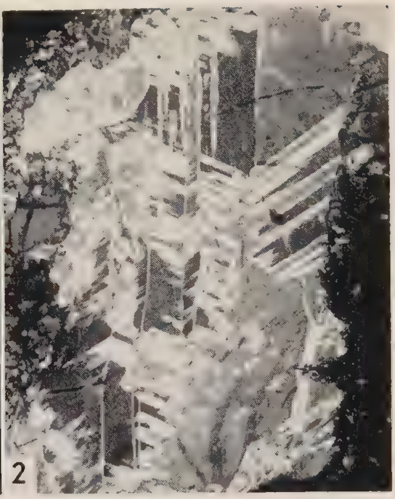

FIG. 2. Interpenetrating lamellae. ×40.

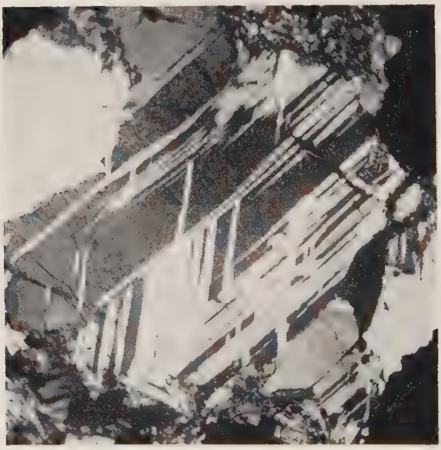

FIG. 3. Interpenetrating lamellae. ×31.

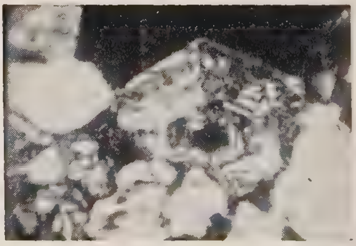

FIG. 4. Concentric twin. ×49.

FIGS. 1 to 4. Photomicrographs of cordierite (all under crossed nicols).

which form a set having identical optical orientation, *i.e.* every third sector is optically similar. This type of pattern is built by a combination of both (110) and (130) twin planes in alternating arrangement. Dittler and Kohler (1938) and Rosenbusch (1905) have recorded indentical forms.

(*b*) Stellate twinning: A more picturesque form of cyclic twinning is the star-shaped pattern. It may be a six-pointed star formed by six rhombs pointing towards the hexagonal sides. This pattern can be built only by similar twin planes and is a modification of the sixling. In the twelve-pointed stellate twin (Fig. 1) there are twelve radiating twin planes which bifurcate towards the periphery and join up with adjacent ones (Venkatesh, 1952*a*).

(*c*) Concentric twinning: A concentric twin pattern results when polysynthetic twin lamellae lie parallel to or at angles of 30° or 60° to the hexagonal outline (Fig. 4). The concentric arrangement can only be superimposed on a radial twin of which it is a further modification. Since polysynthetic lamellae may be arranged parallel or at 30°, 60° or 90° to the two enclosing twin planes in each sector, it is evident that a large variety of concentric twin patterns are theoretically possible; but only a few types have been observed.

Figs. 5 to 8 are diagrammatic representations of twin patterns projected on the basal plane. The slow vibration direction is represented either by arrows or by shading. Optically identical twin units are given same numbers (1, 2 or 3).

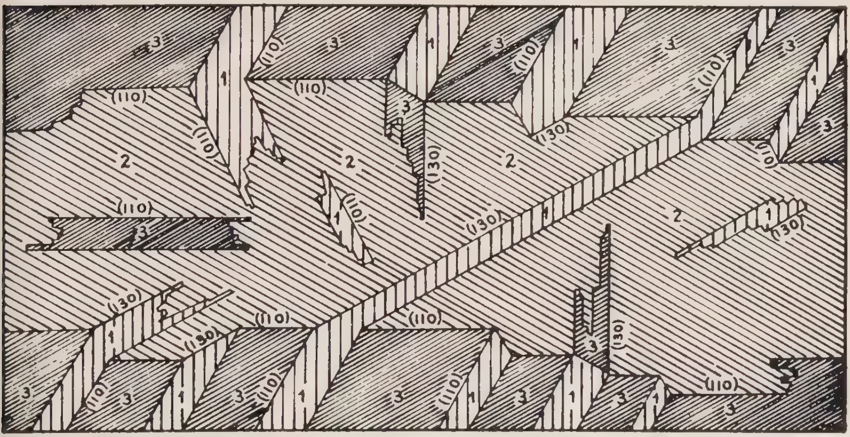

Fig. 5. Relation of interpenetrating lamellae twinned on (110).

A trilling may give rise to a concentric hexagonal pattern which is parallel to the outer periphery. In this case all the twin planes are similar and inclined to one another at angles of 60° (Fig. 6). A triangular concentric pattern is also theoretically possible. Concentric patterns in the sixling may take the form of a hexagon or a six-pointed star. In the former case the concentric hexagonal pattern would look as though it has been rotated by 30° with respect to the hexagonal boundary. The six points of the star-shaped concentric pattern may point either towards the hexagonal corners (Fig. 7) or the sides.

In a twelve-sector twin, the secondary lamellae would form a twelve-pointed star (on the lines of a sixling) or a "dodecagonal" concentric pattern. A hexagonal concentric pattern could also be produced when the secondary twin planes branch off at 90° from the alternate radial twin planes which are normal to the sides of the hexagon. Diverse combinations of the radial, stellate and concentric types yield sometimes a very complex pattern (Fig. 8).

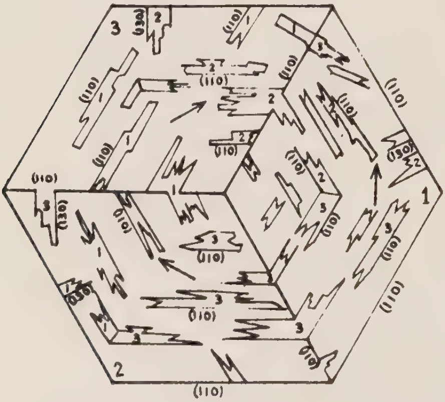

FIG. 6. Concentric hexagonal pattern on a trilling.

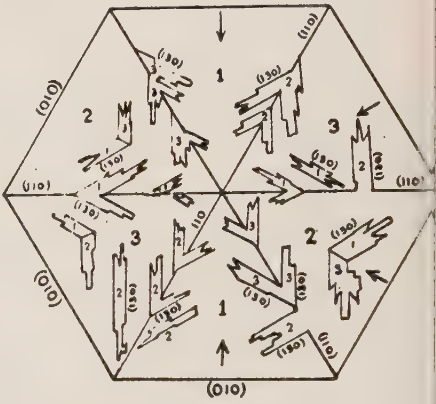

FIG. 7. Star-shaped concentric pattern on a sixling.

Cyclic twinning is confined only to specimen No. 7. Simple trillings and sixlings are rare even in specimen No. 7, whereas the "twelveling" and the twelve-pointed stellate twin are very common. Of the concentric types mentioned above, hexagonal pattern on a twelve-sector twin and a similar pattern modifying a trilling are the only forms observed. In all these the major twin planes pointing towards the outer hexagonal corners are (110), and (130) has never been found in this position.

INTERPENETRATING TWIN LAMELLAE

The following features are seen when two sets of lamellae interpenetrate:

(*a*) When two sets of lamellae enclosed in a common host, cross each other at angles of 30° (*i.e.* twinned on dissimilar planes) or 60° (*i.e.* twinned on similar planes), the following possibilities have been noticed (Fig. 5): (1) One of the lamellae could be cut off against the other, in which case the plane of termination will have to be parallel to either of the vibration directions of the common host. Consequently, the composition plane that truncates the lamella, deviates by 30° or 60° from its original course. (2) But if a lamella is to maintain its optical identity after entering the new surroundings of the second lamella, it has to deviate by 30° or 60° from its course so as to be parallel to either of the vibration directions of the common host. (3) In case a lamella deviates in its course so as to be normal to the composition plane of a second lamella (in which it is enclosed), its identity would become similar to that of the common host.

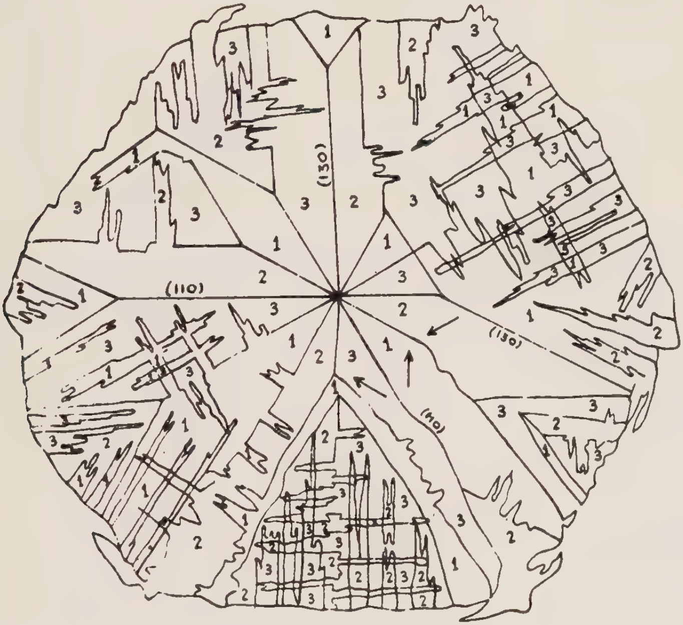

FIG. 8. Complex pattern due to a combination of different types of twinning.

(*b*) When two sets of lamellae enclosed in a common host and twinned on dissimilar planes interpenetrate at 90°, the resulting features are different, as both sets of lamellae have identical optical orientation and only two optically distinct units are present unlike three in the former case. Hence, if the lamellae cross one another, the area of overlap may show the same optical orientation as the common host or be identical with that of the lamellae.

Although in the thin sections examined the interpenetration of lamellae has not been encountered on such a large and prominent scale as to produce a general chequered pattern, minor and limited occurrences of all these variations are convincingly displayed (Fig. 2).

DETERMINATION OF THE TWIN PLANE

The identity of a twin plane could be established with the help of the Universal stage by plotting the X, Y and Z directions and the pole of the twin plane. The trace of the twin plane passes through the X direction; and the angular relations between the poles of the twin planes and the Y and Z directions of the twin individuals, reveal the identity of the twin plane. In simple twins the normal to a (110) twin plane would lie at 30° to the Y vibration direction of the two individuals, and if (130) is the plane, its pole would make similar angles with Z. When two or more similar or dissimilar twin planes are present, the pole of a (110) twin plane would coincide with a Z vibration direction whereas the pole of a (130) twin plane would coincide with a Y vibration direction.

The simplest and most rapid procedure for determining a twin plane in cordierite is as follows. The composition plane is turned north-south and made vertical so that the normal to the plane will coincide with the outer east-west axis of the Universal stage. The microscope stage is then turned to the 45° position and the outer east-west axis is rotated through 50° on either side of the 0° position to find out if the grain shows any extinction. The two individuals would show simultaneous extinction if they are twinned on (110), but if twinned on (130), they would only show equal change in birefringence but not total extinction. This is explained by the fact that the vibration directions do not make angles of 45° with the (130) plane (they make angles of $<30°$ or $>60°$) in any section normal to this plane. But in the case of the (110) plane the vibration directions at some stage make angles of 45° with the trace of the twin plane.

When two or more sets of lamellae inclined to one another are present, the section could be so tilted as to make both sets of planes vertical and sharp. The angular relations of Y and Z with the trace of the twin planes would establish their identity.

Without the Universal stage, identification of twin planes would be difficult unless sections are obtained roughly parallel to the base. But when two sets of inclined lamellae with nearly vertical composition planes are present, the procedure becomes simple. In cases where only one of the two sets of composition planes is sharp, it could be identified by finding whether a fast or slow direction coincides with its normal. Finally, if any twinned grain shows sharp composition planes and roughly symmetrical extinction exceeding 30°, the plane could be readily identified as a (110) plane; but if this extinction is 30° or less, it is of no help in identifying the twin plane.

General Conclusions

Twinning in cordierite seems to be confined exclusively to (110) and (130) planes, and no other twin laws were noticed during the study. Simple twinning and polysynthetic parallel twinning are almost confined to the (110) twin plane. Polysynthetic twinning producing two sets of lamellae inclined at 60° are very common and are all twinned on (110) but never on (130). Combination of (110) and (130) twin planes in prominent interdigitation twins have not been noticed. Lamellar twinning (parallel and interpenetrating) on (110) is by far the most common type of twinning observed. The (110) twin law is exceedingly more common and important than the (130) law. Eskola (1914) has commented on the minor role of the (130) twin plane in cordierite and considers that it is no twin plane at all and strictly not even a composition plane. But this is contradicted by the presence of alternating (130) planes in the "twelveling." It also forms distinct though small and less frequent lamellae.

All the twin planes of similar identity in a twin are either parallel or inclined to one another at angles of 60° or 120° (even multiples of 30°), whereas dissimilar twin planes make angles of 30° or 90° (odd multiples of 30°).

Any twin lamella can make any number of deviations at 90° to its immediate course and still maintain its identity provided it is in the same optical environment. This is also true of any composition plane. In such cases the composition planes oscillate between (110) and (130) at every turn. Repeated deviations of this nature on a submicroscopic scale would explain the bulging and thinning of lamellae and the curved and irregular nature of the twin planes so often seen.

The type of twinning found in cordierite seems to bear some relation to the nature of the rock in which it occurs. It is noteworthy that simple and polysynthetic twinning are the most common types in coarse to medium grained, gneissic or granular rocks where larger grains of cordierite generally occur. Some examples of sixlings and trillings in cordierites from gneisses, pegmatites, etc. have been recorded in the literature but no instances were found in the rocks studied. Cyclic twinning producing the complex radial and concentric patterns, are totally unrepresented in the rocks mentioned above and have been observed only in specimen No. 7 (vitrophyre) and similar petrographic types formed under comparable conditions (Hussak, 1883 and Venkatesh, 1952*b*). The synthetic cordierite crystals from melts studied by Shand (1943), Dittler and Kohler (1938), and Richardson and Rigby (1949) are described as showing highly complex twin patterns and idiomorphic outlines. The common presence of simple cyclic twins and sometimes complex modifications of it in some hornfelses and other pyrometamorphic rocks, has been repeatedly recorded in the literature.

It appears, therefore, that cyclic twins and the many complex modifications of it are common in, and characteristic of, cordierites which have formed under conditions of high temperature or from melts. On the other hand, cordierites from granular or coarse-textured rocks which have not been subjected to such high temperatures during their growth history, seldom show the complicated forms, but show sometimes the simple sector twins and most commonly the simple and polysynthetic types of twinning. Gorai (1951) has recorded similar evidence regarding the influence of temperature on the type of twinning in the case of felspars.

ACKNOWLEDGMENTS

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SPECTROGRAPHIC EXAMINATION OF THE OCCURRENCE OF CERTAIN ALKALI ELEMENTS IN CALCITE MARBLES

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Abstract

More than 100 samples of calcite marbles were analyzed spectrographically by the line width method for three alkali elements: sodium, potassium, and lithium. Sodium content varied from 0.001 to 0.067%, potassium content from <0.005 to 0.43%, and lithium content from none to 0.0018%. Rubidium was found only in four marbles in trace amounts. A geographical pattern was discernible. Statistical resolutions of the errors showed the film error to be somewhat greater than the analytical, and both errors combined were found to vary from one-half to one-fifth of the sampling error. In spite of pronounced scattering, a general potassium-sodium relationship of 5:1 was observed. Where potassium was 0.2% or higher, trace amounts of rubidium were detected.

Introduction

In the course of some exploratory examinations of marble samples from commercial quarry beds throughout the United States considerable variations in the sodium and potassium content were observed. It was thought that knowledge of the alkali content from a wide selection of samples might be helpful in some geological and weathering interpretations.

Spectrographic Anlaysis

Spectrographic analysis is ideally suited to this problem for several reasons: (1) Four alkali elements (lithium, sodium, potassium and rubidium) are detectable in a single spectrographic exposure range. (2) A single sample can be completely analyzed in much less time than is required for a sodium determination by chemical methods. (3) Such small amounts of these alkalis were present in most of the samples that the use of chemical methods would not have been sufficiently sensitive.

The spectral phenomenon of self-reversal is particularly strong in the alkali elements and always enters the problem of analysis when more than ten times the detectable limit is present. Self-reversal, an effect which produces the so-called Fraunhofer or dark lines in the solar spectrum, is due to the absorption of some of the emitted light by the colder vapors surrounding arcs and flames. It causes the intensity of certain spectral radiations to be abnormally diminished. Consequently any concentrations determined from peak intensity measurements of such absorbed lines will be low. Dilution of the samples down to a normally useable range would have entailed a great deal of survey work and subsequent errors for the large number of samples to be analyzed. The line width method has been used for various problems where self-reversal has been present (Coheur, 1946, Eastmond and Williams, 1948). In this method a trace of the line is made by a Leeds and Northrup microphotometer from which the line width at 60% transmission is measured and used as a function of the concentration present. This technique can be used over a concentration range of more than 2000 fold while the usual procedure is useful for about a 20 fold range.

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ANALYTICAL PROCEDURE

A series of standards was made to contain 0.003%, 0.01%, 0.03%, 0.1%, and 0.3% sodium and potassium and 1/10 of those amounts of lithium. The base material was calcium carbonate precipitated from c.p. calcium nitrate solution and washed more than 30 times with hot, deionized water (Archibald, 1932). A residual correction method indicated that 0.001% sodium was present (Nachtrieb, 1950). This amount was compensated for when plotting working curves of log *line widths* vs. log *concentrations*. The presence of no other alkalis was detected in the calcium carbonate base.

Samples selected for analysis were crushed and ground to pass a 100-mesh bolting cloth sieve. High purity graphite electrodes, 6.3 mm. in diameter with 2 mm. deep center post craters, were packed level with standard or sample material and burned in a 300-volt direct current arc at 12 amperes for 60 seconds. Spectra were recorded by an Applied Research Laboratories two-meter grating spectrograph on Eastman Spectroscopic Film type I-L. A Wratten K-2 filter was placed at the slit to absorb the interfering radiations. The camera was positioned so that the following lines were recorded whenever they were present: sodium 5889.95 Å, lithium 6707.84, potassium 7664.90, and rubidium 7800.23. Cesium, which has a relatively poor sensitivity, has lines that occur beyond the wavelength range of the spectrograph at the camera setting for sodium. Consequently the presence of cesium was not sought.

OBSERVATIONS

Information was desired as to the magnitudes of the film and experimental errors and as to the size of these two errors as compared with the sampling error. To obtain the former, a large number of spectra were made of two different samples, and the statistical results of one sample, Vermont Imperial Danby marble, are shown in Table 1. The other sample, Tennessee Ross Pink marble, indicated comparable precision. The results and accompanying analyses of variance are given in Table 1.

TABLE 1. PRECISION OF DETERMINATIONS OF SAMPLE OF VERMONT IMPERIAL DANBY MARBLE

	Sodium Analyses			
	Film A	Film B	Film C	Film D
	0.0072	0.0064	0.0072	0.0072
	0.0092	0.0092	0.0086	0.0058
	0.0092	0.0090	0.0072	0.0072
	0.0092	0.0060	0.0078	0.0098
	0.0088	0.0092	0.0064	0.0072
Film Averages	0.0087	0.0080	0.0074	0.0074
Sample Average	0.0079 per cent sodium			

Analysis of Variance of Sodium Determinations

Variance Associated with	Degrees of Freedom	Variance	F Ratio	1% Level Critical F Values
Films	3	0.00000180	2.03	4.5
Analyses	4	0.00000110	1.24	4.0
Experimental Error	29	0.000000886	—	—

	Potassium Analyses			
	Film A	Film B	Film C	Film D
	0.074	0.060	0.067	0.058
	0.064	0.059	0.069	0.060
	0.078	0.060	0.078	0.064
	0.077	0.055	0.073	0.070
	0.079	0.055	0.069	0.064
Film Averages	0.074	0.058	0.071	0.063
Sample Average	0.067 per cent potassium			

Analysis of Variance of Potassium Determinations

Variance Associated with	Degrees of Freedom	Variance	F Ratio	1% Level Critical F Values
Films	3	0.000285	4.0	4.5
Analyses	4	0.000033	0.46	4.0
Experimental Error	29	0.000072	—	—

In making an analysis of variance (Youden, 1951), the error associated with the four different films in Table 1 was calculated and found to be less than the critical F value in comparison with the experimental error at the one per cent confidence level for both sodium and potassium. The variance associated with the analyses was lower than the film variance; for potassium the low analytical F ratio reflects the much greater differences among the films for that element. The relative magnitudes of the F ratios show, with one chance in a hundred of being incorrect, that the errors are not large enough to be the result of chance and can be relied on to that extent.

Resolution of the errors was continued by investigating the sampling error. Thirty-seven samples of three calcite marbles were analyzed in triplicate or in duplicate and the magnitudes of the errors were established in terms of the standard deviations, as shown in Table 2. It is apparent that the sampling error was two to five times the film and analytical errors combined.

TABLE 2. RESOLUTION OF ERRORS FOR THREE CALCITE MARBLES

State	Name of Marble	Number of Samples	Number of Analyses	Element Found	Averages, Per Cent	Standard Deviations, Per Cent	
						Film+ Analytical	Sampling
Alabama	Cream	12	24	Na	0.0060	0.00141	0.00280
				K	0.026	0.0038	0.0068
Georgia	Creole	12	36	Na	0.011	0.00083	0.0042
				K	0.015	0.0025	0.0138
Georgia	White	13	26	Na	0.0038	0.00118	0.00172
				K	<0.001	—	—

The samples were selected at random, in order to minimize bias, from a large number of freshly-quarried marble samples cut from three mutually perpendicular directions in the quarry beds. The trade names have been utilized for identification of the marbles since the color, grain size, and textural patterns associated with the names are adhered to quite closely by the industry. After intensive analyses to establish the magnitudes of the errors for the three marbles discussed above, the investigation was broadened to include as large a number of marble varieties as possible.

Duplicate determinations were made and averaged to furnish sample

State of Origin	Name of Marble	Number of Sample	Potassium				Sodium				Lithium
			Average	Standard Error	Low Sample	High Sample	Average	Standard Error	Low Sample	High Sample	Average
Alabama	Cream	12	0.026	0.002	0.016	0.037	0.0060	0.0005	0.0031	0.0097	<0.0001
	Madre Cream	1	0.016	—	—	—	<0.001	—	—	—	<0.0001
	Madre Veined	1	0.042	—	—	—	0.0059	—	—	—	N.D.
	Madre Veined	1	0.46	—	—	—	0.030	—	—	—	0.0018
Georgia	Creole	12	0.015	0.007	<0.005	0.072	0.011	0.001	0.0074	0.022	<0.001
	White	13	<0.001	—	—	—	0.0038	0.0005	0.0023	0.0074	N.D.
	White Cherokee	3	<0.003	—	<0.003	<0.003	0.0092	0.0014	0.0065	0.0111	N.D.
	Silver Gray	1	<0.005	—	—	—	0.0077	—	—	—	N.D.
	Etowah	3	0.073	0.035	0.035	0.145	0.047	0.008	0.032	0.058	N.D.
Missouri	Ozark Tavernelle	6	0.035	0.003	0.024	0.042	0.012	0.001	0.0096	0.015	<0.0001
	Ozark Veined	1	0.055	—	—	—	0.014	—	—	—	<0.0001
	St. Genevieve Rose	1	0.041	—	—	—	0.013	—	—	—	<0.0001
	St. Genevieve Golden Vein	1	0.019	—	—	—	0.019	—	—	—	<0.0001
Vermont	Imperial Danby	7	0.081	0.018	0.010	0.145	0.012	0.003	0.0030	0.027	0.0001
	Standard White	3	0.17	0.01	0.16	0.18	0.0068	0.0027	0.0030	0.012	0.0001
	Brocadillo	6	0.24	0.01	0.20	0.30	0.042	0.007	0.025	0.067	0.00072
	Westland Cippolino	6	0.34	0.06	0.24	0.43	0.082	0.007	0.054	0.10	0.0011
	Verdoso	1	0.40	—	—	—	0.027	—	—	—	0.0013
	Metawee	1	0.093	—	—	—	0.0068	—	—	—	0.0001
	Pearl	1	0.21	—	—	—	0.0018	—	—	—	0.0008
	Clarendon Light Exterior	1	0.083	—	—	—	0.0084	—	—	—	<0.0001
	West Rutland White Exterior	1	0.040	—	—	—	0.0043	—	—	—	N.D.
	Pittsford Italian	1	0.047	—	—	—	0.0080	—	—	—	<0.0001
	Pittsford Valley	3	0.053	0.005	0.045	0.062	0.0066	0.0005	0.0058	0.0078	N.D.
	Neshobe	1	0.020	—	—	—	0.0051	—	—	—	N.D.
	Neshobe Gray	3	0.0083	0.0016	0.0023	0.018	0.016	0.001	0.0032	0.0070	N.D.
	West Blue	1	0.026	—	—	—	0.0058	—	—	—	<0.0001
Tennessee	Ross Pink	3	0.014	0.002	0.0070	0.027	0.053	0.003	0.014	0.023	<0.0001
	Cedar Tavernelle	3	0.11	0.006	0.10	0.12	0.018	0.001	0.017	0.019	0.0002
	Granox Quaker Gray	3	0.040	0.009	0.029	0.058	0.057	0.002	0.0016	0.022	0.0002

N.D. = Not Detected.

means. When the values deviated from the mean by more than 25%, redeterminations were made and used. The results are tabulated in Table 3 for sodium, potassium, and lithium. The rubidium line 7800.23 Å indicated trace amounts in the spectra of only Alabama Madre Veined, Vermont Brocadillo, Vermont Westland Cippolino and Vermont Verdoso marbles. It is worth mentioning that the samples in which the potassium was 0.2% or higher also contained rubidium in detectable amounts. The confidence limits of the sample average can be obtained by multiplying the standard error as given in Table 3 by the desired confidence interval. The standard error was computed using the equation

$$s_{\bar{x}} = \sqrt{\frac{\sum(\bar{x} - x_i)^2}{n(n-1)}},$$

where

$\bar{x}$ = arithmetic mean,
x_i = single sample,
n = number of samples.

It was observed, upon plotting the sample means of sodium vs. potassium on log-log paper, that there was a general relationship in which the potassium was for the most part five times greater than the sodium. Scattering was pronounced, however, and a few individual cases showed ratios varying between 0.5 and 50. A general geographical pattern was observed. The Georgia samples ran less than 0.01% sodium and very low in potassium, thus causing a strong divergence from the five to one ratio for potassium-sodium noted above. The Alabama marbles with one exception were quite low in sodium. Vermont samples in general showed a high concentration of alkali elements.

SUMMARY

Over 100 samples of calcite marbles have been analyzed for sodium and potassium by measuring the width of the spectral line. It was observed that the alkali content followed a pattern depending on the geographical origin. In general, where sodium was high, potassium showed a ratio of 5:1. Where potassium was above 0.2%, the presence of rubidium was observed in four cases.

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A NOTE ON THE HYDROTHERMAL SYNTHESIS OF SINGLE CRYSTALS OF SILICATES AND OTHER ROCK-FORMING MINERALS*

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Abstract

Single crystals of eucryptite as well as of numerous other minerals have been recently synthesized. The general technique involves placing the various components of a desired phase in separate compartments in a bomb and heating them under moderate to high pressures of water vapor. The materials diffuse together and solid phases nucleate and grow. The rate of availability of various metal components to a growing phase is very markedly a function of the *pH* of the solution.

During the last several years the writer has synthesized a considerable number of crystals of various silicates and other rock-forming minerals in crystals of sufficient size for goniometric and single crystal x-ray work. Among these have been various beryllium silicates, end members of feldspars, some micas, and a series of lithium-aluminum silicates, one of which is to be described in a forthcoming paper by M. Mrose. This note on the general method involved is presented with the thought that it may be of interest to mineralogists concerned with working out the properties of imperfectly crystallized naturally occurring minerals, and who are dissatisfied with the material nature sometimes provides.

The basic method is that of high pressure-high temperature hydrothermal synthesis, although the equipment involved is relatively simple. A bomb, the preferred design of which is shown in Fig. 2, is connected by means of a length of stainless steel capillary tubing to a pressure gage. Pressures may be obtained by partially filling the bomb with water before heating, or by connection to a pump. The bomb is heated in a thermostated furnace of convenient dimensions. The details of this bomb and its construction have been presented elsewhere (Kennedy, G. C., 1950). Bombs of this design, if made of appropriate materials, may be safely operated to temperatures of 800° C. and pressures of 2000 atmospheres.

The first step is that of the selection of the proper pressure temperature interval in which to carry out the synthesis. In general, rates of recrystallization of most minerals, exclusive of the sulfides, are extremely slow at temperatures below 400° C. Temperatures in the range of 500° to 700° C. may be satisfactorily used for most pegmatite minerals and vein minerals, providing the mineral under investigation does not have pressure sensitive polymorphs and does not contain a volatile. In general, also, the highest possible water pressure produces the most rapid recrystallization and the best growth, as the solvent power of superheated steam is essentially in proportion to its density.

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Special problems are encountered in the synthesis of minerals which have pressure sensitive polymorphs. Well known examples of these are the transitions involving graphite-diamond, kyanite-andalusite, andalusite-sillimanite, kyanite-sillimanite, quartz-tridymite, albite plus nepheline-jadeite, and many others. Most of these are transitions of the *A*-*B* type shown in Fig. 1, where the boundary line between the stability fields of *A* and *B* is essentially a straight line extending to higher pressures at higher temperatures, although examples of transitions with negative slopes are known. The slope of this line is equal to $\Delta H/T\Delta V$ where ΔH is the heat of the transition, T is the temperature and ΔV is the volume change of the transition. The boundary curve between two minerals showing this type of transition will be *absolutely* straight only if the heat capacities and the compressibilities of the two phases remain unchanged with changes in pressure and temperature, or in case the changes, as they affect the terms ΔH and ΔV, exactly cancel each other out. Neither of these conditions exactly hold, but, over the range of possible laboratory experimental operations, hold as close first approximations. It is obvious that in order to bring about transition of phase *B* to phase *A*, combination of either high temperatures and high pressures or low temperatures and low pressures is required. Many difficulties are

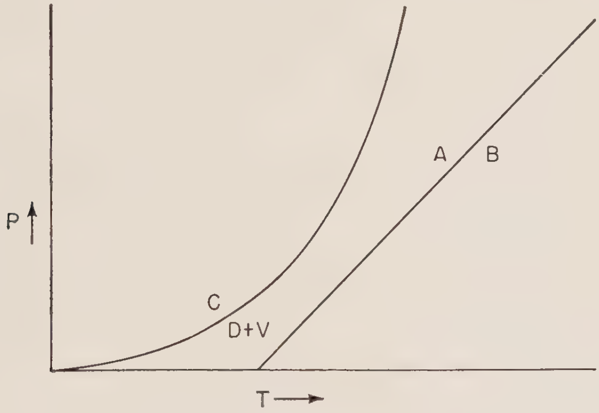

FIG. 1. Types of stability fields in a pressure versus temperature plot.

encountered in successfully bringing about these transitions. In many cases the rate of the transition is so slow at low temperatures as to make the transition impractical. Apparently the transition rate of graphite to diamond, phase *A* on our diagram, approaches zero at room temperature, even though the appropriate pressure be applied to graphite to bring it into the diamond stability field. Correspondingly, at the high temperatures where the reaction rate is appreciable, the pressure required to be in the stability field of phase *A* may be beyond that readily obtainable in the laboratory at the high temperatures. By contrast, however, transitions in the reverse direction, from *A* to *B*, are readily brought about in most cases by heat alone or heat in conjunction with some fluxing agent such as water.

Minerals which contain a volatile generally have stability fields of a somewhat different shape and have field boundary curves as shown in Fig. 1 of the *C-D* plus volatile type. In reactions of this class, the pressure axis of the graph shown in Fig. 1 is not the pressure on the mineral, but rather the partial pressure of the volatile involved at a transition temperature. High confining pressure on the mineral, in addition to the pressure of the volatile on the mineral, generally pivots the boundary curve in a lower temperature direction. The volatile involved in such a reaction may be CO_2, as in the case of quartz plus calcite→wollastonite plus carbon dioxide. CO_2 is involved in similar reactions for all the carbonate minerals.

Analogous reactions are found in most of the minerals which contain water. Among these reactions are such common ones as pyrophyllite →sillimanite plus water, paragonite→albite plus water, muscovite→orthoclase plus sillimanite plus water, etc., as well as a host of much more complex reactions such as those involved in the transition of amphiboles to pyroxenes. Boundary curves of this shape also delineate the stability fields of such simple reactions as those in which a mineral goes from one state of hydration to another, as in the case of nickel sulfate heptahydrate→nickel sulfate hexahydrate.

Similarly shaped boundary curves separate the stability field of the various sulfide minerals. At a given temperature most sulfide minerals are stable over only a very limited range of sulfur vapor pressures. At a higher sulfur vapor pressure the mineral reacts to form a mineral or minerals of higher sulfur content. At a lower sulfur vapor pressure, the mineral reacts to form a phase or phases of lower sulfur content. This may be done experimentally in the laboratory and characteristic "replacement" textures result. In this regard it is interesting to note that the usual paragenetic sequence observed in the sulfide minerals is the same sequence as is obtained by arranging the minerals in order of descending sulfur vapor pressure at a given temperature.

The equation of the field boundary curve of the *C-D* plus volatile type is again the Clapeyron equation of the form $dP/dT = \Delta H/T\Delta V$. Over the low volatile pressure range of the boundary curve, the equation of state for the ideal gas, $PV = RT$, may be substituted in the ΔV term neglecting the volume of the solid phase, thus the equation simplifies to the form $ln\ P = \Delta H/RT + C$, where C is the integration constant. At higher pressures much more complex formulations result, as the gases, such as water, depart sharply from ideality and the volume of the solid cannot be conveniently neglected. Existing gas data are sufficient, however, so that for most purposes only a single point on the curve need be determined experimentally and the position of the remainder of the curve may be computed with adequate accuracy.

The fact that hydration-dehydration reactions in the silicates must show a boundary curve of the *C-D* type is not fully appreciated by some of the present workers in the field of hydrothermal experimentation. An example of this is in recent work on the system alumina silica-water. This writer, in collaboration with G. J. F. MacDonald, has determined the transition pressure of the pyrophyllite-mullite reaction. The experimentally determined points are reasonably close to calculated values and theory and experiment are in accord. However, a recent paper, shows this as a reaction taking place at a temperature of 575° C. at all water pressures, ranging from 2000 p.s.i. (130 bars) to 28,000 p.s.i. (1900 bars). Such results could only approximately obtain if the volume of water vapor involved in the reaction were independent of pressure; whereas actually volume changes several fold in magnitude take place over this pressure interval.

It is significant to note that the vapor pressure, with which a crystal containing a volatile is stable, only becomes zero at a temperature of zero on the absolute scale, though the reaction rate may be negligible at temperatures as high as 600° absolute. Were there no carbon dioxide in the air, for example, and if the reaction rate was sufficiently rapid, calcite with quartz would be metastable and would break down to form wollastonite at room temperature.

The problems, therefore, in synthesizing crystals of these substances are obvious. At temperatures of 500° C. to 600° C. where rates of crystal growth are rapid, very large water pressures or pressures of some other gas may be required to reach the stability field of some of the volatile containing silicates. Conversely, difficulty is encountered in synthesizing some of the anhydrous silicates by hydrothermal means. If the vapor pressure of water is maintained high enough to promote rapid recrystallization, the hydrated phase may be obtained. This indeed is the problem in kyanite synthesis. Water vapor pressures of more than a few atmospheres, at temperatures where kyanite is presumed to be stable, will produce the hydrated phase pyrophyllite. For such cases, a solvent other than water must be found.

The techniques of producing single crystals of a mm. or more in dimensions are relatively simple for most minerals once the stability field of the mineral has been found, providing that temperatures of 400° to 700° C. may be employed and water pressures of 1000 to 2000 atmospheres are usable. A stoichiometric mixture of the finely powdered oxides is generally first prepared and held at temperature and pressure in the bomb for a few days. At the end of this time the bomb product is examined either microscopically or by *x*-ray techniques. If the reaction runs in the right direction, the product is generally made up of exceedingly fine crystals, for maximal nucleation is present under such conditions. Occasionally crystals of a millimeter or more result, but more usually the powder emerges from the bomb as a cake of crystallites.

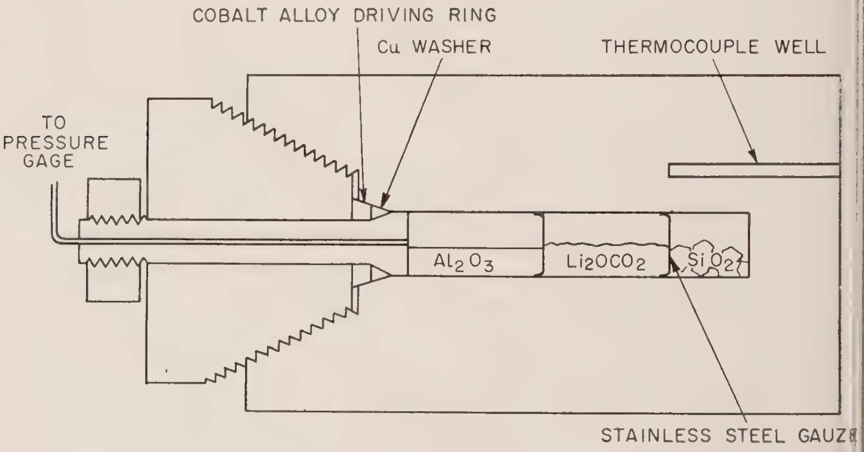

FIG. 2. Bomb showing arrangement of ingredients in eucryptite synthesis.

The bomb is next compartmented by the use of platinum or stainless steel gauze, as is illustrated in Fig. 2 for the case of the eucryptite synthesis. The various ingredients are placed in the separate compartments. The object of this arrangement is to force the various oxides to migrate by solution and diffusion in the dense hot water vapor to a common center or centers, where the appropriate phase will form and nucleate out. Such an arrangement greatly cuts down the number of crystal nuclei formed. A small number of larger crystals are formed instead of a large number of small crystals. Ingerson and Tuttle (1947) have described an arrangement, different in detail but similar in principal, used in the synthesis of single crystals of willemite. Though a single phase may form when a stoichiometric mixture is used, the common result is that a large number of different phases will form under the conditions as described above. In the case illustrated, a series of phases, rich in lithium to poor in lithium, including eucryptite, were found extending from the lithium end of the bomb to the aluminum end of the bomb. At least two of these phases yielded optical and *x*-ray data unlike those of any compounds for which the writer could find data in the literature. These may well have been metastably formed compounds.

In many syntheses it is desirable to speed up or slow down the rate at which certain ions are available to the growing crystal. Rate at which silica is made available to the growing crystal, for instance, may be readily controlled by varying the grain size of the silica at its source in the bomb. The silica supply may range from amorphous powdered silica to a single lump of crystalline quartz. If alkali is tolerable in the system, NaOH or KOH will greatly step up the rate at which silica is available.

The rate at which the metals ions is made available can be controlled by varying the *pH* of the solution used in the bomb. A few drops of HCl will permit volatile metal chlorides to form which readily move by diffusion in the dense vapor. This does not seem always desirable in the case of some of the aluminum silicates, where, under slightly acid conditions, the supply of aluminum may be so great that spontaneous nucleation is extremely rapid near the silica source, and large numbers of small crystallites are formed. It is to be remembered that aluminum is amphoteric, and under such conditions a neutral or weakly acid solution appears to give the best results. The use of acid solutions, particularly at high temperatures and low pressures, present many problems. Under these conditions, a chemically inert liner, generally platinum, must be used to protect the bomb walls from excessive corrosion and the sample from contamination. With such an arrangement, crystals of various metal oxides may be grown readily, but here silicates are exceedingly difficult to grow, for silica appears to be of very slight solubility in low pressure acid gases.

It is thus possible in most cases, by careful attention to *pH* and to the state of subdivision of the starting ingredients, to obtain an arrangement whereby the desired single crystals will grow at an appreciable rate and spontaneous nucleation may be held to a minimum. In the case of the eucryptite synthesis, coarse lumps of quartz were used for the silica supply, aluminum hydroxide was used for the aluminum supply, and lithium carbonate for the lithium supply. The dry bomb was first brought to temperature, 600° C., with the pressure line open. This served to permit dissociation of some of the lithium carbonate to lithium oxide plus carbon dioxide. Before the dissociation had gone to completion, however, the pressure line was connected to the bomb and the pressure brought to 2000 atmospheres by pumping in water. The resulting solution was weakly acid as some CO_2 continued to be evolved by the lithium carbonate. The bomb was held at temperature and pressure for one week. The run contained several of the lithium aluminum silicates, all well crystallized. Among the phases present was eucryptite in crystals 1 to 2 mm. length.

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NOTES AND NEWS

POLLUCITE FROM LITHIA, MASSACHUSETTS

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The discovery of pollucite in western Massachusetts by the senior author in the autumn of 1940 adds another locality to the rather short list of known sources for this cesium-rich mineral. At the time the mineral was discovered he and Mr. Alvan Barrus, a son of the present owner, were engaged in blasting some of the loose boulders at the site of the well-known Barrus pegmatite in the town of Goshen.

The close similarity in appearance of pollucite to quartz, and especially to goshenite, probably accounts to some extent for the relatively few occurrences reported to date. The mineral is undoubtedly rather rare, but probably has been frequently overlooked. The usual association of pollucite is with lepidolite, spodumene, tourmaline—colorless and colored varieties, quartz and cleavelandite, together with a number of rare pegmatite minerals. This mineral association in sodium-lithium rich pegmatites may be taken as an indication of the possible presence of pollucite.

The initial discovery at the Barrus pegmatite yielded a relatively small amount of the pollucite which occurred in irregular grains several inches across. Although the large grains were usually intimately fractured in more or less rectangular pieces or relatively thin plates, parts of the grains were essentially clear and colorless. All of the fractured surfaces were bounded by good conchoidal fractures. Associated with the pollucite were quartz; colorless, pinkish, and greenish spodumene; colorless, blue, green, and pink tourmaline; cleavelandite; muscovite—often fringed with a pink color; cassiterite; columbite; goshenite; and several clay minerals. In this pegmatite, lepidolite is rare or absent which appears to be an exception for the associated minerals of pollucite.

In the spring of 1946, another boulder containing 25 to 50 pounds of pollucite was located and broken to free the pollucite masses. The surface of this boulder, about 2 to 2½ feet in diameter, contained an exposed mass of pollucite occupying approximately ½ square foot in area. The appearance of the pollucite on the surface of the boulder is so characteristic as to make its presence on the surface of other boulders readily recognizable. The specimen represented in Fig. 1 shows such a mass of pollucite weighing slightly less than 5 pounds. It is traversed by a series of veins following a somewhat irregular arrangement of roughly parallel or en echelon fractures as well as a few cross-cutting ones, all of which stand out sharply in strong relief. Most of the veins are filled principally with spodumene together with some mica and clay minerals. The spodumene grains are positioned normal to the veins walls. The smaller veins are composed in large part of halloysite. Microscopic examination of the spodumene in the veins shows it to be unaltered and to contain an intricate system of intergrown vermicular quartz. On the surface of the veins the minute quartz inclusions are exposed and present a multitude of hard, sharp points which easily abrade the pointed end of a small file and readily remove a dense streak of the metal when drawn across the grains.

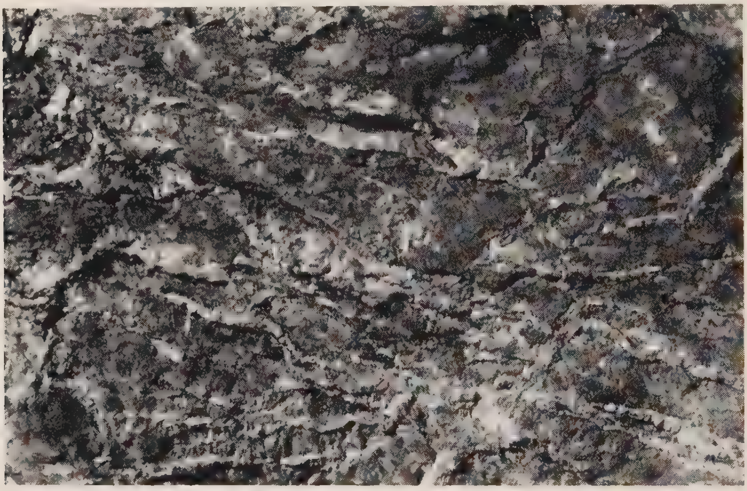

FIG. 1. Weathered surface of pollucite exposed on the surface of a boulder. Note the irregular veins of spodumene with some mica which stand out sharply in relief.

In sections cut across the pollucite and veins, one sees a sharp contact between all of the vein minerals and the pollucite. There is no replacement of the pollucite by any of the vein minerals. In many of the broken pieces of pollucite, the thin clay films or veins, usually of halloysite, separate readily from the pollucite and clearly reveal the original conchoidal fractured surfaces. All such pieces have a matte surface instead of the vitreous to subvitreous luster of the freshly broken pieces. This matte surface may be caused either by a very slight etching or by a thin coating left by the clay.

During the centuries that the boulder was exposed to weathering, the badly fractured pollucite was gradually removed in small pieces by the many cycles of freezing and thawing. The vein minerals were, on the other hand, less susceptible to the same disintegrating action. None o the associated minerals show any appreciable alterations traceable t weathering. At a number of places the pollucite is intricately broken int small pieces and the fractures are filled with clay in a manner which give the appearance that the pollucite was altering to clay. Again the conchoidal fractured surface of the pieces of pollucite and its freshness are evidence to the contrary. This is apparently the first instance where the effect of recent weathering on pollucite in a loose boulder has been noted.

The physical properties of the pollucite were determined with considerable care for comparison with those of the mineral from other localities. The specific gravity is 2.975 and the index of refraction is 1.520. The dimension of the unit cell as computed from x-ray diffraction data is 13.65 Å. These values check very closely with those for pollucite from both Hebron and the Tamminen pit in Maine.

Hardness of pollucite—The apparent low hardness of the pollucite from the Barrus pegmatite as compared with the published value of 6.5 which is given in several texts incited a further interest in this property. Since the pollucite could be easily scratched with a small pointed file while feldspar could not be scratched in this manner except under very heavy pressure, it was at once obvious that pollucite was much softer instead of harder than feldspar. The pollucite readily scratched the Durango, Mexico, apatite but could not be scratched by it. A polished surface of sanidine, on the other hand, could not be scratched by pollucite although the former readily scratched the latter. From these comparisons along with the relative ease with which pollucite and apatite can be scratched with a file, the hardness of the pollucite from the Barrus pegmatite was determined to be of the order of $5\frac{1}{4}$ to $5\frac{1}{2}$. Hardness tests were likewise made on pollucite from Uncle Tom's Mt., Greenwood, Maine, and from the Nevel mine, Newry, Maine. In both instances the hardness is close to $5\frac{1}{2}$. Hence, it appears that the published hardness of pollucite is at least a full scale division too high.

The low hardness of pollucite makes it possible for anyone to identify the mineral in the field with a piece of quartz, always at hand, as the latter will readily scratch the pollucite but will not scratch any of the minerals that could be mistaken for it.

In examining the data on pollucite from the principal localities as shown in Table 1, it is to be noted that the ones richest in cesium are also those having the highest index of refraction and specific gravity. The pollucite from the Barrus pegmatite has both a high index of refraction, 1.52, and a high specific gravity, 2.975, hence it would be expected that it contains a relatively high percentage of cesium.

Although the Barrus pegmatite appears to be relatively small at the surface, the presence of spodumene in considerable amounts together with pollucite in sizeable masses offers an inducement for further exploration to determine whether they are present in commercial amounts.

TABLE I

Locality	% Water	% Cs_2O	Index of Refraction	Specific Gravity	Hardness	Unit Cell in Å
Hebron, Maine (1)*	1.50	36.10	1.5247 (Na)	2.98		
Tamminen pit, Greenwood, Maine (2)	1.62	35.83	1.522	2.97		13.65
Mount Mica, Maine (2)			1.520	2.90		
Elba (2)	2.40	34.30	1.520	2.90		13.66
Buckfield, Maine (2)			1.520	2.90		
Greenwood, Maine, Small crystals (2)	3.80	24.48	1.507	2.68		13.64
Leominster, Massachusetts (2)	2.04	33.06	1.520	2.89		13.65
Karibib, South West Africa (3)	2.66	30.2	1.517	2.86		
Varutrask, Sweden (4)	1.80	30.77	1.5218	2.917		
Black Hills, South Dakota (5)	3.45	23.46				
Lithia, Massachusetts			1.520	2.975	5¼–5½	13.65

* Numbers indicate the references from which the data were obtained.

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AN INEXPENSIVE MICROSCOPE ILLUMINATOR

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The lamp herein described was designed for use with the petrological microscope when an inexpensive source of both transmitted and reflected light is desired. As may be seen in the photographs, the illuminator has two units. The lower unit provides excellent illumination for all purposes requiring the use of transmitted light, while the upper one produces illumination permitting observation of articles on the stage by reflected light. By means of the switch at the right one may be simultaneously turned on and the other extinguished.

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Details of Construction

The photographs show the general appearance of the illuminator. The details of the front face and right side will be found in Fig. 1. The internal arrangement of parts may be seen in Fig. 2.

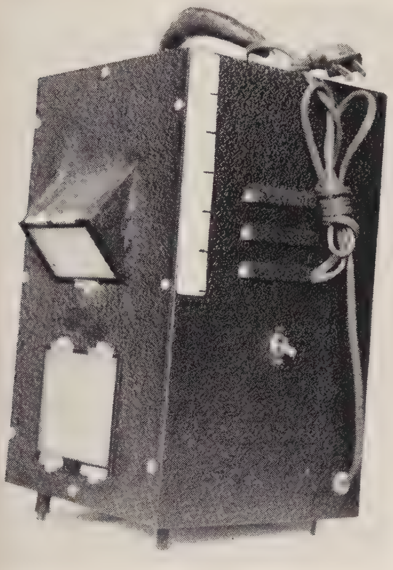

Fig. 1. General view of illuminator. Scale in figure is 6 inch ruler.

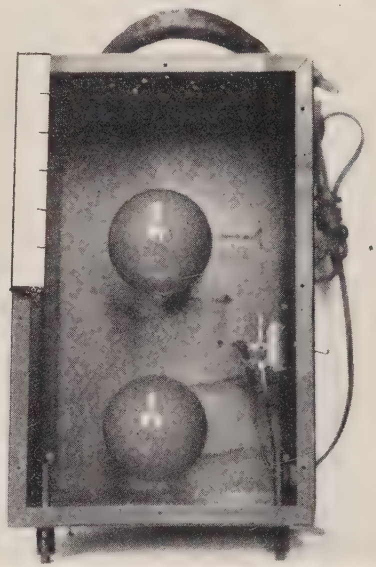

Fig. 2. Internal arrangement of parts. Scale in figure is 6 inch ruler.

The unit operates on 110–125 volts A.C. It is simple and inexpensive to build and operate. The total cost was $6.11. The size of the cabinet is $12'' \times 7\frac{3}{4}'' \times 7''$ but may be reduced considerably in every dimension if so desired. A complete parts list will be found at the end of this article. Many of the smaller parts are scrap for which other materials may be substituted.

Care should be exercised when cutting out the material to form the opening for the lower illuminator since this material may later be used to provide the triangles which are the sides of the upper light shield. The angles of these triangles are not critical since the unit may be mounted on legs which may be made easily of any reasonable diameter screws of any length over $\frac{3}{4}''$. These may be made adjustable by means of two nuts, one inside and one outside the cabinet. Additional refinements may include permanent $\frac{3}{4}''$ rear legs and adjustable front legs which are merely bakelite (or brass) rods set in shaft collars which are soldered to the cabinet. All soldering should be done with a 1000 watt iron or, if available, a small spot welder.

Blue daylight 100 watt lamps are used. The lamp windows are merely frosted window glass. The mountings, in this case, were cut from the plates of an old variable electrical condenser; however, small aluminum plates are quite satisfactory since they easily may be shaped to fit the angles required.

Electrically, the unit consists of two circuits, one on each side of the switch wired in parallel to the center terminals of a double-pole-double-throw toggle switch. Figure 3 is a schematic diagram of the electrical circuit involved. The wire used should be no smaller than number 14 and placed carefully so as to prevent the possibility of shorting out the circuit. Wire of the above diameter or larger will be rigid enough to stay in place.

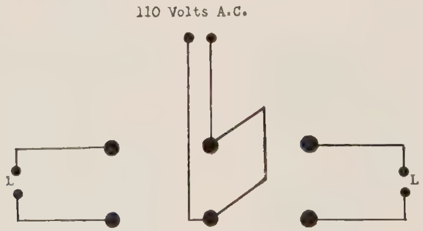

FIG. 3. Schematic wiring diagram. L = lamp socket.

It may be noted that the cabinet as listed is provided with louvres to remove internal heat. However, it is advisable to drill a series of small holes both on the top and bottom of the case in order to increase air circulation.

The parts list which follows includes all items bought by the author. Much of it may be found in scrap boxes and thus will reduce the total cost. Parts mentioned in the text which are not found in the list were scrap materials the author had on hand but total cost would not be over fifty cents.

PARTS LIST

Parts	*Current Price*
1 metal cabinet, I.C.A. type 3850 12″×7¾″×7″	$2.84
2 110 volt lamp sockets—16 cents each	.32
5 ft. of 2 conductor cable	.15
1 DPDT toggle switch, Cutler-Hammer type 7561-K4, 15 A., 125 V., bat handle	.85
1 6″×8″ window pane	.15
1 roll ¾″ No. 33 "scotch" electrical tape (black)	.55

2 daylight, blue, lamps—33 cents each	.66
1 bottle No. 145, Walsco touch-up paint, black	.39
1 110 V. A.C. male plug	.10
5 ft. No. 14 copper wire, enameled	.10
Total Cost	$6.11

The described illuminator enables a rapid change from transmitted to reflected light which is convenient for the examination of the opaque accessories in thin sections. The use of this illuminator eliminates the necessity of handling a rather warm lamp when a source of reflected light is required.

The author wishes to express his gratitude to Dr. F. Donald Bloss for his aid in the preparation of this paper.

LANTHANON AND SCANDIUM DISTRIBUTION IN WESTERN AUSTRALIAN FERGUSONITE

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Hand-picked fergusonite of detrital origin from the Marble Bar district of northern Western Australia has been found to contain a high proportion of ytterbium and erbium and a small proportion of scandium. The identity of the metamict material was established by optical, *x*-ray and differential thermal (1) examination, the results being confirmed by chemical analysis (2, 13):

Ta_2O_5	Nb_2O_5	TiO_2	Fe_2O_3	Y_2O_3	Ln_2O_3*	U_3O_8	ThO_2
49.4	2.70	2.50	<0.1	21.2	12.0	0.30	0.13%

* Total lanthanons.

Though the customary name for this material has been used it may be noted that the term 'formanite' is proposed in Dana's "*System of Mineralogy*" for material containing preponderating amounts of tantalum (3). The low thorium and uranium content of the Marble Bar product is notable and serves to differentiate it from material of otherwise similar composition from the neighbouring district of Cooglegong (4).

The lanthanon-yttrium fraction was examined spectrophotometrically and by chemical means as described elsewhere (5, 6, 7).

La_2O_3	Ce_2O_3	Pr_2O_5	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3*
0.05	2.0	1.4	5.7	8.5	5.7	8.6%
Tb_2O_3*	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3*
1.7	11	3.1	15	4.3	27	5.7%

* Approximate values.

The distribution thus shows a maximum abundance in the region erbium-ytterbium, that is, towards higher atomic numbers than reported by Goldschmidt and Thomassen (8) for complex oxide minerals containing tantalum and niobium. A somewhat similar distribution was reported by Sahama and Vähätalo (9) for wiikite, and by Dixon and the writer for the heavy lanthanon fraction of davidite (10).

The widespread occurrence of scandium and its sporadic enrichment in lanthanon minerals has been qualitatively demonstrated by Eberhard (11). According to Rankama and Sahama (12) scandium if present in such minerals is markedly concentrated only in those varieties containing a high proportion of ytterbium and lutetium, that is, of lanthanons with small atomic radius. A search for scandium was therefore made, in which the mineral was decomposed in hydrofluoric acid and scandium separated by the cellulose column technique of Kember (13) or the thiocyanate extraction procedure of Fischer and Bock (14). Provided preliminary separations involving filtration of tantalum and niobium oxides were avoided, scandium could be detected in the solvent extracts by means of ammonium tartrate (14, 15) and sodium alizarin 3-sulphonate (14, 16). These results were confirmed spectrographically. Adsorption of all or part of the scandium occurred on "acid earth" precipitates. Tests with alizarin 3-sulphonate and pure scandium, yttrium and thorium salts enabled the amount of scandia in the extracts to be assessed at approximately 0.02%, more accurate estimation by chemical means being hindered by the lack of published information on the chemistry of scandium.

The author wishes to thank Miss M. Mercovich, Dr. T. R. Scott, Mr. A. D. Wadsley and Mr. A. G. Sussex for assistance with experimental work.

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WEBERITE FROM PIKES PEAK, COLORADO

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The mineral collection of the Cryolite Company: "Kryolitselskabet Øresund" A/S, Copenhagen, Denmark, contains two specimens labelled "Cryolite, Colorado ?, *A* and *B*." They are about 3 cm. across and consist of a grayish-white, fine-grained mass, the single grains being less than 0.3 mm. in diameter. A specimen much larger than these, about 12 cm. across, but without any label, was found together with other mineral samples, and as it is essentially of the same type as the first-mentioned specimens, it must be assumed that *A* and *B* represent fragments of the larger piece. This assumption may be considered quite safe, judging from the singular character of the specimens.

The collection of the Mineralogical Museum of the University of Copenhagen contains a specimen similar to those mentioned above. It is labelled: "Cryolite, St. Peter's Dome, Colorado, 1903, no. 1364; donated by C. F. Jarl" (former President of the Cryolite Company). Under no. 1364, the catalogue of that collection, in addition to the text on the label, bears the statement: "magnesium-containing cryolite." Even though the four specimens differ a little, their general character warrants the assumption that they all came from the same locality.

A comparison with material from the Urals did not show any such similarities. In Ivigtut no material has ever been found which showed relations or textures such as are to be seen on the Colorado material.

A. H. Nielsen, chemist at the Cryolite Company, called my attention to the unusual composition of the two specimens *A* and *B*, which he had analyzed some time ago. The results are shown in table 1.

The high content of Mg is scarcely compatable with a mineral like cryolite, and A. H. Nielsen suggested that weberite or one of the "cubic" minerals known from Ivigtut might be present. The microscopic examination clearly showed that at least three quarters of the material was weberite. The mineral has an index of refraction between 1.345 and 1.350, it is biaxial with a large axial angle and corresponds closely to the material described by R. Bøgvad (1938) from the Greenlandic occurrence at Ivigtut.

The literature was searched but nothing was found indicating earlier observations of Mg in cryolite from Pikes Peak. In order to establish the

TABLE 1

	1	2	3	4	5	6	7	8	9	10	11
Insoluble*	0.24	—	—	—	—	2.90	4.10	0.17	1.51	0.10	0.16
Al	13.45	21.03	11.92	11.71	14.3	12.97	12.94	12.23	11.77	13.55	13.25
Ca	none	—	—	—	—	1.44	1.32	5.77	6.43	0.39	0.46
Mg	10.02	5.55	10.80	10.56	8.6	7.59	6.84	8.56	8.58	9.45	9.54
Fe	none	—	—	—	—	—	—	0.26	tr.	0.27	0.25
Na	18.81	7.44	20.87	19.97	18.3	15.84	19.50	—	15.82	—	18.77
K	—	—	—	—	—	—	—	—	tr.†	—	none
F	55.07‡	46.26	56.41	57.76	(58.7)	53.43	(55.30)	ca 54.8	—	ca 56.6	—
H_2O	2.30	14.26	(none)	none	—	5.78	—	—	3.14	—	1.92
Total	99.89	—	100.00	100.00	(99.9)	99.95	—		—	—	—

* In 1, 8, 9, 10, 11, Ti has been determined qualitatively.

† Revealed by means of a hand-spectroscope, H. Pauly.

‡ Determined by H. Buchwald.

1. "Cryolite" from Colorado. Min. Mus. Copenhagen. Analyst A. H. Nielsen.
2. "First cubic mineral" from Ivigtut. Analyst, H. Buchwald 1935.
3. 1. recalculated after deducting 16.13% of 2.
4. Weberite theoretical.
5. "Colorado-Cryolite," analyst, C. F. Jarl 1897.
6. "Colorado-Cryolite," analysis from Pennsylvania Salt Co. 1902.
7. "Colorado-Cryolite," analysis from "Øresund" 1903.
8. Sample *B* labelled Colorado Cryolite ?, analyst, A. H. Nielsen.
9. Sample *B* labelled Colorado Cryolite ?, analyst, A. H. Nielsen.
10. Sample *A* labelled Colorado Cryolite ?, analyst, A. H. Nielsen.
11. Sample *A* labelled Colorado Cryolite ?, analyst A. H. Nielsen.

origin and the locality of the samples and the way in which the Cryolite Company had acquired them, H. Buchwald, chief chemist of the chemical laboratory of the Cryolite Company, and A. H. Nielsen searched the records of the company. It was then revealed that in 1897 C. F. Jarl made an analysis of a sample of cryolite from Colorado with the result listed under no. 5 in the table. As Jarl was on a journey to the United States in 1896, we may assume that he himself brought home the sample he examined. He gives the figures for the fluorine compounds, here recalculated to the elements (F presumably calculated as F bound to the other components). This would seem to be the first observation of Mg in "cryolite."

In the year 1902, the Cryolite Company received a letter from the Pennsylvania Salt Manufacturing Company, Philadelphia, U.S.A., containing an analysis which was said to represent the cryolite ore from the Rocky Mountains. This analysis is given under no. 6 in the table. The following year, 1903, this company received a larger sample of the ore for a closer examination. Another analysis was then made (listed under no. 7). It may be assumed that when Jarl received larger amounts of the material he decided to give part of it to the Mineralogical Museum in Copenhagen, and this is probably the specimen mentioned above.

Upon the whole it may be concluded from a study of the earlier letters that the ore body of Pikes Peak was of a relatively large size and, what seems to be essential here, the content of Mg must be rather large; in other words, the mineral weberite plays an important part in the occurrence.

From the description given by Cross and Hillebrand, these specimens may be said to have come from the socalled "Eureca" tunnel where the vein *B* of the above-mentioned authors is located. On page 290 of their paper they describe the fluorides from this place as follows:

"The greater part of the fluoride mass is now dull white and very compact, and is evidently made up of a mixture of at least two substances, neither of which has as yet been identified. Only in a single specimen is there any clue to the original mineral, but in that there is a small, solid mass of unmistakable cryolite with alteration to pachnolite (?) progressing upon its cleavage planes in the exact manner described in vein *A*, but passing into the compact white mixture already mentioned."

This may be taken to mean that Cross and Hillebrand really observed weberite and the other minerals, but were not then able to determine the new mineral.

Together with the weberite several other minerals are observed: rutile, as fine needles included in the weberite grains, and in some of the samples scattered in it as black elongated grains up to 1 mm. in length. This agrees well with the observed Ti in the analyses. Thomsenolite and/or pachnolite may be present in a few grains. In *B* which contains large amounts of Ca, fluorite occurs, and here also prosopite is present. This also points to the "Eureca" tunnel or vein *B* as the most probable place of origin for the weberite.

In this connection it may be of interest to add some information I received from H. Sørensen. During his work on systematic *x*-ray powder photography of minerals (carried out in Oslo for Dr. H. Neumann), weberite together with prosopite were found in a sample labelled Prosopite, Colorado. Dr. Neumann has kindly let me have the specimen, which belongs to the mineral collection of Oslo Mineralogical Museum, for comparison with the material discussed here. I take this occasion to express my very cordial thanks to Dr. Neumann. On one side, the sample has a coarse-grained aggregate of greenish prosopite, whereas the other side is very much like the samples found in our collections. Microscopically the sample is seen to contain the same minerals.

Among the most interesting minerals found with weberite in all the samples are three "cubic" minerals. They constitute about 15 percent of the material. The refractive indices of these minerals are near 1.365, 1.390 and 1.41. The determinations may vary about 5 in the third decimal. Judging from the refractive indices they may be compared with some minerals from Ivigtut described by O. B. Bøggild in 1913 as the third "cubic" mineral and the first "cubic" mineral.* The mineral having an index near 1.41 may be ralstonite. The third "cubic" mineral is only known from a steamboiler in Ivigtut, the second is known to occur together with thomsenolite in Ivigtut.

The term "cubic" is used in spite of the minerals being clearly but weakly anisotropic, because these minerals from Ivigtut have been classified as cubic.

The problems connected with ralstonite and the "cubic" minerals from Ivigtut have been studied for some time, and a closer examination of these relations, carried out on Ivigtut material, will be finished in the near future in this laboratory in collaboration with the staff of the Mineralogical Museum. R. Bøgvad,† late chief geologist to the Cryolite Company, started these investigations together with H. Buchwald. As it is of interest here, an analysis of the first "cubic" mineral, carried out by Buchwald, has been given here with his kind permission (no. 2 in the table). Bøgvad gives $n=1.406\pm0.001$. Bøggild (1913) for his first "cubic" mineral gives $n=1.3852$. The Colorado mineral has n about 1.390. They do not agree very closely, but the following seems to justify the similarity: Assuming that all the water in the analysis given under no. 1 represents water from a "cubic" mineral with a composition as given under no. 2 in the table, Buchwald calculated the amount of "cubic" mineral present and subtracted it in the analysis and recalculated the rest at 100 per cent with the result as listed under no. 3. As will be seen, this gives a fairly good agreement with the theoretical composition of weberite as set forth as no. 4 in the table. Accordingly the analyzed sample from the Mineralogical Museum in Copenhagen contains 84 per cent of weberite and 16 per cent of a "cubic" mineral. This is in good agreement with the microscopic results.

Analyses 8 to 11 have been included in the table just to show the variations in the material.

During his stay at the Oslo Mineralogical Institute, H. Sørensen was so kind as to make some x-ray powder diagrams of different types of weberite from Ivigtut and of some of the Colorado samples. The patterns are almost identical. A slight difference represented by some extra lines in the Colorado material may be due to an admixed "cubic" mineral, but this is not immediately evident. As these lines are very weak no weight has been attached to their occurrence.

From the microscopic examination of thin sections it is evident that the "cubic" minerals have replaced the weberite. The texture exhibited by these minerals is seen in Fig. 1. It may perhaps constitute a valuable guide in the studies of these minerals and their relations as well as their structural behavior.

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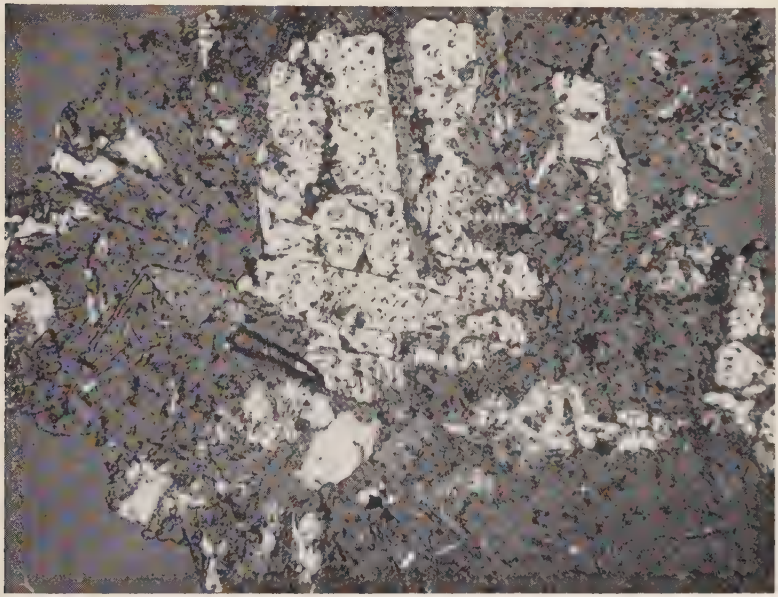
* By O. B. Bøggild termed "regular" minerals in "The Mineralogy of Greenland."

† He died in 1952, while working in the neighborhood of Ivigtut.



A thin section of Pikes Peak material, in liquid with $n=1.347$. Weberite crystals corroded by "cubic" minerals. Mag. 134×. Upper nicol a few degrees from crossed position in order to show the surrounding material.

It may be of interest to mention that the sections were made in the ordinary way, but afterwards the balsam was removed and pieces of a section were imbedded in a mixture of water and glycerol having an index near those of the minerals, in order to avoid too great a relief.

SUMMARY

An examination of certain samples from the cryolite deposit, Pikes Peak, Colorado, has shown that weberite, hitherto only known from Ivigtut, is to be found among the minerals there, and that it occurs together with three different "cubic" minerals, resembling the first and third "cubic" minerals from Ivigtut, and ralstonite.

By kind permission of H. Tuxen, President of "Kryolitselskabet Øresund" A/S, I have been able to publish these investigations. For this I offer my best thanks.

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A DISCUSSION ON "ORIENTED OLIVINE INCLUSIONS IN DIAMOND"

P. Hartman, *Rijks. University, Groningen, Netherlands.*

Recently Mitchell and Giardini (1953) reported on oriented inclusions of olivine in diamond flats. The orientation was such that (010) of olivine was parallel to (111) of the diamond and that the zone [101] of olivine was parallel to [101] of the diamond. The inclusions were elongated parallel to the [101] direction which was common to both the olivine and diamond. This is a very peculiar habit for olivine crystals as they are commonly elongated parallel to the *c*-axis. However, this habit can be understood on the basis of a newly developed theory of crystal morphology (Hartman and Perdok, 1952). According to this theory the habit of a crystal is governed by a set of chains of strong bonds running through the structure. Such a periodic bond-chain is represented by a periodic bond chain vector (P.B.C. vector) with a length equal to the period of the attachment energy of the chains.

Oriented inclusions are always connected with the pseudo-equality of parameters. In the present case the pseudo-equality concerns the direction [101] in both crystals. For the diamond the cube edge length is 3.56 Å. (Wyckoff, Chap. II, table p. 11). The parameters for olivine are: $a = 4.77$ Å, $b = 10.28$ Å, and $c = 6.00$ Å (*Strunz, Min. Tabellen,* p. 169). The axes chosen here are the morphological ones. From these data [101] for the diamond is 5.03 Å and [101] for olivine is 7.66 Å, that is nearly $3/2 \times 5.03$ (misfit 1.5%). This is a good agreement. In the diamond the direction [110] makes with [101] an angle of 60°. In olivine the direction $[\bar{1}02]$ makes with 101 an angle of 60°8′ and its length is 12.91 Å, that is approximately 5/2 times 5.03. The misfit is here 2.5%. According to Neuhaus (1943) oriented inclusions should have pseudo-equality of parameters in three dimensions. In this case it is found that the *b*-axis of olivine is exactly equal to $5 \times d_{111}$ of the diamond.

Now it can be concluded from an inspection of the structure of olivine that there are P.B.C. vectors connected with *a.o.* [001] and [101]. The zone [102] is not a P.B.C. vector. Hence it follows that if a very small crystal of olivine is oriented on (111) of the diamond as described by Mitchell and Giardini, it can easily grow in the direction [101], but not in other directions. The zones [001] and [$\bar{1}$01] do not fit well on the substrata and although these directions are represented by P.B.C. vectors, the growth velocity in these directions is relatively small. Therefore, the crystals are elongated only parallel to the zone [101]. As the olivine crystals are included in the diamond, this process has occurred during the growth of the diamond. It is not possible that the olivine crystal settled down in full-grown state on the diamond, because in that case the direction of elongation would presumably have been [001], certainly not [101]. (Conclusion that the diamond grew at a temp. $<$ melting point of olivine?)

Similar deviations from the normal habit have been reported in the literature. Frondel and Ashby (1937) mention hematite crystals that have grown as needles on muscovite. Recently Watanabe and Ueda (1953) showed an electron micrograph of octahedral antimony oxide formed on a cleavage surface of stibnite, in which the senarmontite is elongated parallel to the zone [110].

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A SECOND LOCALITY OF NOVACEKITE

T. W. Stern and C. S. Annell, *U. S. Geological Survey, Washington, D. C.*

Novacekite, $Mg(UO_2)_2(AsO_4)_2 \cdot nH_2O$, recently described by Frondel (1951, p. 680) from Schneeberg, Saxony, has been identified from the Woodrow area, Laguna Reservation, Valencia County, New Mexico. This member of the torbernite group was collected in August 1952 by L. B. Riley, E. S. Erickson, Jr., and T. W. Stern, of the U. S. Geological Survey, who had been conducted to the locality by R. M. Coudray of the Anaconda Copper Mining Co. The novacekite, straw yellow in color, coats a somewhat iron-stained friable sandstone in the Westwater Canyon sandstone member of the Morrison formation of Jurassic age.

Novacekite forms a series with saléeite, $Mg(UO_2)_2(PO_4)_2 \cdot 10H_2O$, its phosphate analogue. Frondel divides this phosphate-arsenate series and applies the species name novacekite to the half in which As $>$ P in atomic per cent and the species name saléeite to the half in which P>As in atomic per cent. A specimen near the phosphate end of the series has been analyzed (Thoreau and Vaes, 1932, p. 96; Mrose, 1950, p. 528), but no specimens near the arsenate end of the series have been analyzed. A semiquantitative spectrographic analysis of the New Mexico material (by C. S. Annell, of the U. S. Geological Survey) indicated As_2O_5 in the greater-than-10-per cent bracket, but P_2O_5 was not observed in any bracket down to a sensitivity limit of 0.1 per cent. The amount of material present in this specimen was not sufficient for a quantitative chemical analysis.

The x-ray powder pattern of novacekite differs from the patterns of saléeite and arsenian saléeite only by its slightly larger unit-cell dimensions. The unit-cell dimensions of arsenian saléeite are $a_0 = 7.05$Å, $c_0 = 19.87$ Å and of novacekite, $a_0 = 7.20$ Å, $c_0 = 20.22$ Å.

Optically this material is anomalously biaxial negative with $\alpha = 1.625$, $\beta = 1.641$, $\gamma = 1.641$, and 2V 5 to 20°. This specimen is pleochroic with X colorless, Y pale yellow green, and Z pale yellow green. Its specific gravity is 3.7. The mineral fluoresces bright lemon yellow in both short and long wavelength ultraviolet radiation.

This work was completed as part of a program undertaken by the U. S. Geological Survey on behalf of the Division of Raw Materials of the Atomic Energy Commission.

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ARROJADITE IS A FERROAN DICKINSONITE

D. Jerome Fisher, *Department of Geology, University of Chicago, Chicago 37, Illinois.*

While working on classifying my x-ray powder films of the pegmatite phosphate minerals, it was recently noted that arrojadite from the Black Hills and dickinsonite from Branchville, Conn., yielded substantially identical results. In her recent paper (3) Mrs. Lindberg compared the powder photos of arrojadite with those from a number of other pegmatite phosphates, but not with dickinsonite. Figure 1 shows prints from my two films.

TABLE 1. CHEMICAL ANALYSES

	Dickinsonite			Arrojadite		
	1	2	3	4	5	6
K_2O	1.52	1.80	1.73	1.74	2.00	1.45
CaO	2.15	2.09	2.01	2.46	5.53	5.69
Na_2O	7.46	7.37	7.41	6.40	7.46	4.67
MnO	31.58	31.83	31.83	15.78	15.54	12.33
FeO	13.25	12.96	12.33	28.22	25.05	19.84
Fe_2O_3				none	none	12.39
MgO	tr	none	1.67	1.04	1.50	1.85
Li_2O	0.17	0.22	0.20	0.09	0.28	tr
SnO_2						1.52
Al_2O_3				2.66		
P_2O_5	39.57	40.89	40.78	40.00	38.64	34.32
H_2O	1.65	1.63	1.82	0.91	0.73	5.40
F				0.80	0.69	
Insol.	2.58	0.82	1.00	0.11	2.47	0.66
Total	99.93	99.61	100.78	100.21	99.89	100.12
Less O=F				0.34	0.23	
				99.87	99.66	

1–2. Dickinsonite, Branchville, Conn. Wells, *Am. Jour. Sci.*, **39,** 213 (1890).
3. Dickinsonite, Poland, Me. Gonyer, *Am. Mineral.*, **15,** 381 (1930).
4. Arrojadite, Black Hills. Lindberg, *Am. Mineral.*, **35,** 69 (1950).
5. Arrojadite, Black Hills. Headden (see Lindberg).
6. Arrojadite, Serra Branca. Guimarães (see Lindberg, p. 68).

Table 1 lists chemical analyses of the two minerals taken from the literature. Particular attention is called to nos. 3 & 4, since they represent the only available modern analyses of fresh material. These are very similar if it is noted that $MnO+FeO=44.08\pm0.08$.

Crystallographic data taken from Wolfe (4) and Mrs. Lindberg are as follows:

TABLE 2

	Space Group	a_0	b_0	c_0	β	Volume	Meas. Grav.
Dickinsonite	$C\,2/c$	16.70	9.95	24.69	104°41′	3968	3.55
Arrojadite	$C\,2/m$	16.60	10.02	23.99	93°37′	3982	3.42

The only serious discrepancy is in the β-angle; the writer expects to do single crystal work to check these values.

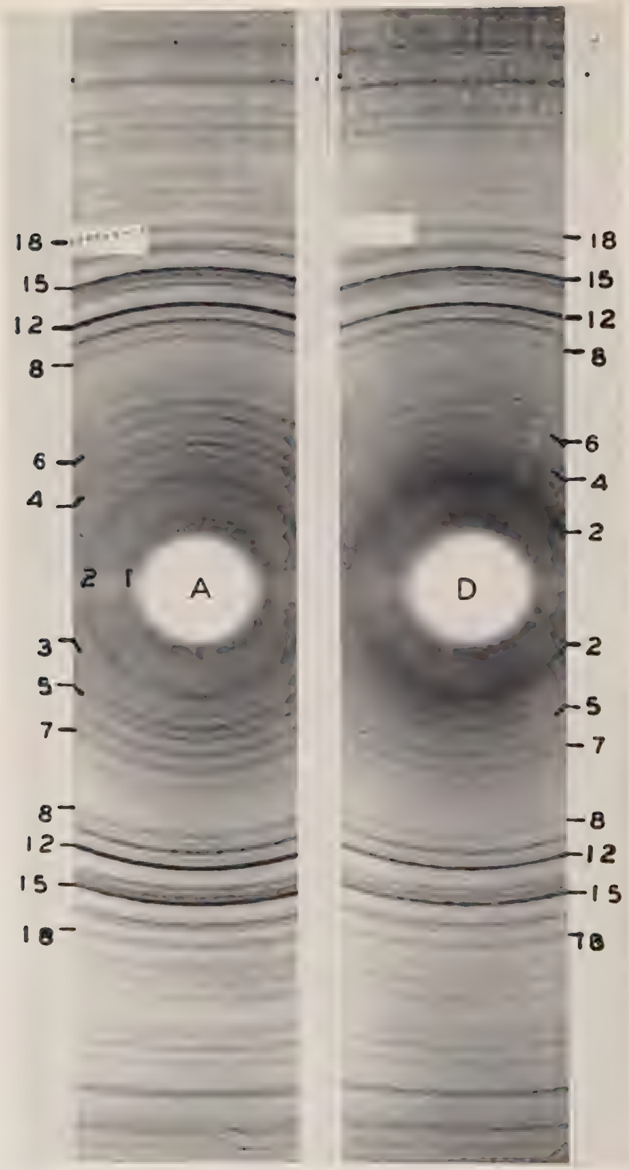

FIG. 1. *X*-ray powder photos, Fe radiation (Mn filter), 114.6 mm. diam. camera, natural scale. Some of the lines are numbered as in Table 3.

A—Arrojadite, Nickel Plate Mine, Black Hills, South Dakota. The crushed sample (prepared from a specimen in the Headden Collection of Harvard University) was kindly supplied by M. L. Lindberg of the U. S. Geological Survey.

D—Dickinsonite, Branchville, Conn. The sample is from Yale University (Brush Coll. 3090) through the courtesy of Professor Horace Winchell. It consists of dark green platy crystals lining a small vug in lithiophilite (altered to sicklerite near the vug).

Table 3. Arrojadite X-ray Data (See Fig. 1)

No.	Lindberg (3)		Fisher*			
	I	d	I	$d_{\text{meas.}}$	$d_{\text{calc.}}$	Indices
1	2	12.14	2	11.82	11.92	002
2	3	7.62	3	7.62	7.59	201†
	1	7.12				
3	2	6.52	2	6.48	6.51	202
4	4	5.93	4	5.93	5.96	004
					5.90	$\bar{2}03$, $\bar{1}13$
5	4	5.54	3	5.52	5.50	203, 104‡
					5.48	300
6	3	5.01	4	4.99	5.01	020, $\bar{2}04$‡
					4.96	$\bar{1}14$
7	3	4.58	3	4.58		
7*a*	1	4.23	(Skip one faint line)			
	1	3.84				
8	3	3.42	3	3.410		
9	1	3.33	1	3.313		
10	6	3.22	7	3.212		
11	2	3.13	1	3.118		
12	10	3.04	10	3.037		
13	4	2.85	5	2.846		
14	4	2.77	5	2.766		
15	8	2.72	9	2.703		
	1	2.68	(skip 2 faint lines)			
	1	2.59				
16	3	2.56	5	2.553		
17	2	2.518	2	2.505		
18	2	2.424	4	2.415		

---

* Spacings measured by Leon Atlas; indices computed by A. A. Forslev using the technique of Bloss (1) and the cell data of Lindberg (3).

† 201 is an impossible reflection according to the space group criteria of Wolfe (4) for dickinsonite from Poland, Me.; so are $\bar{2}03$ and 203.

‡ These two indices are impossible reflections according to space group criteria.

The formulas given (using one of the alternatives listed by Mrs. Lindberg) are as follows:

Dickinsonite	
System II 718 (from Wolfe)	$4[H_2Na_6(Mn, Fe, Ca, Mg)_{14}(PO_4)_{12}\cdot H_2O]$
Arrojadite	
System II 680	$12[Na_2(Fe'', Mn'')_5(PO_4)_4]$
Lindberg	$4[(Na, K)_5(Fe, Mn, Ca)_{16}(PO_4)_{12}(F, OH)\cdot H_2O]$.

These will be discussed in a later report.

The optical data (2) agree in showing $\alpha \sim\!\!\longrightarrow [b]$, a very large 2V, and for dickinsonite $\beta\wedge[c] = +15°$, while for arrojadite $\beta\wedge[c] = +21°$; indices of refraction are a bit higher in arrojadite, as is to be expected from its higher iron content.

It is concluded that the name *arrojadite* should be dropped in favor of *ferroan dickinsonite*, since the latter term has a 47-year priority.

Note: The indices and calculated spacings listed in Table 3 are erroneous, since they are based on an incorrect unit cell. Wolfe has chosen the correct cell, but his numerical results are slightly small; β is 105°52′.

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METEORITICS: THE JOURNAL OF THE METEORITICAL SOCIETY AND THE INSTITUTE OF METEORITICS OF THE UNIVERSITY OF NEW MEXICO

From the time of the inception of the Meteoritical Society in 1933, its *Notes* and *Contributions* were published regularly in the monthly magazine, *Popular Astronomy*, until December, 1951, when that periodical was discontinued on the completion of its 59th volume. By arrangement with the University of New Mexico and by unanimous vote of the Council of the Society, a new publication entitled *Meteoritics: The Journal of the Meteoritical Society and the Institute of Meteoritics of the University of New Mexico* was established, and its premier issue, consisting of 25 items and 123 pages, appeared in December, 1953, as Volume 1, Number 1, Whole Number 1, 1953.

Meteoritics is to be issued at least once but not more than four times a year. It is expected that eventually the journal will become a quarterly. Each volume is intended to contain from 240 to 360 pages. The Editor of the Meteoritical Society, Dr. Frederick C. Leonard of the University of California, Los Angeles, is the Editor of *Meteoritics*, and the Director of the Institute of Meteoritics of the University of New Mexico, Dr. Lincoln La Paz, is the Associate Editor.

The annual subscription price of *Meteoritics*, to both members and non-members of the Meteoritical Society, is $4.00 (or, to student members, $2.00), regardless of the number of issues published. Orders for subscriptions should be sent to the Secretary of the Meteoritical Society, Dr. John A. Russell, Department of Astronomy, University of Southern California, Los Angeles 7, California.

Dr. William J. McCaughey, Professor emeritus of the Department of Mineralogy at Ohio State University, was named the 1954 recipient of the Albert Victor Bleininger Award. The award is the highest honor conferred in this country for "distinguished achievement in the field of ceramics" and is given annually by the Pittsburgh Section.

The presentation was made on March 12, 1954.

Lawson H. Bauer, chief chemist and mineralogist of the New Jersey Zinc Co., died Jan. 27, 1954, in the Franklin Hospital, Franklin, New Jersey, at the age of 65 years.

The following are the officers of the Society of Exploration Geophysicists for 1954-55:

President: Paul L. Lyons, exploration manager of Anchor Petroleum Company, Tulsa, Oklahoma.

Vice-President: Roy F. Bennett, chief geophysicist of Sohio Petroleum Company, Oklahoma City, Oklahoma.

Secretary-Treasurer: Hugh M. Thralls, Vice-president of Seismograph Service Corporation, Tulsa, Oklahoma.

Editor: Milton B. Dobrin, Magnolia Petroleum Company, Dallas, Texas.

The Fifth International Colloquium on Spectroscopy will be held at Gmunden (Salzkammergut, Austria), August 30–September 3, 1954. The sections on absorption and emission spectroscopy will be held as usual. It is proposed to deal preferably with the application of molecular spectroscopy to the examination of artificial fibers. With reference to emission spectroscopy it is suggested that the discussion be devoted to the analytics of nonconductors and the alloys of copper.

Errata

Volume 39, page 143, date of manuscript received should read "Jan. 29, 1953," instead of "Jan. 29, 1954."

MINERALOGICAL SOCIETY (LONDON)

A meeting of the Society was held on Thursday, January 28th, 1954, at 5 p.m., in the apartments of the Geological Society of London, Burlington House, Piccadilly, W.1. (by kind permission).

The following papers were read:

(1) THE STRUCTURES OF THE PLAGIOCLASE FELDSPARS. V. THE HEAT TREATMENT OF LIME-RICH PLAGIOCLASES.

By Dr. P. Gay.

A number of lime-rich plagioclases have been subjected to varying heat treatments; the effects of these heat treatments have been studied by *x*-ray single crystal methods.

It is found that appreciable changes occur after severe heat treatments. Two important conclusions can be reached from the examination of the experimental data. First, partially inverted materials can exist stably, and so the concept of unique high and low temperature series is incorrect. Secondly, at least for feldspars from 0–80% An, the high temperature form shows a *c*-axis length of 7Å, similar to that of the albite structure. This, take together with the fact that the intermediate feldspars can be homogenized by heating t give a 7Å *c*-axis, suggests that at high temperatures a range of solid solutions exists fro albite almost up to pure anorthite. This resolves the apparent discrepancy between pr vious *x*-ray investigations and the early thermal work.

(2) INVESTIGATION OF THE CRYSTAL STRUCTURE OF ANTIGORITE FROM MIKONUI, NEW ZEALAND.

By Dr. J. Zussman.

A variety of antigorite from Mikonui, New Zealand, was examined by Aruja (*Mi Mag.*, 1944, vol. **27**, p. 65), and found to have cell dimensions $a=43.5$, $b=9.26$, $c=7.28$ Å., $\beta=91.4°$.

A crystal of this variety has now been found which gives clearer *x*-ray diffraction photographs than those hitherto obtained, so that a Weissenberg ($h0l$) layer could be indexe completely and the intensities measured visually.

Trial structures based upon kaolinite type sheets, corrugated in different ways, have been tested most conveniently by comparing the "optical transforms" of their "*b*" axis projection with the *x*-ray data.

(3) THE IDENTITY OF JURUPAITE AND XONOTLITE.

By Dr. H. F. W. Taylor.

Jurupaite, discovered by Eakle in 1921 at Crestmore, California, is shown by *x*-ray powder and oriented fibre photographs to be identical with xonotlite ($3CaSiO_3$. H_2O) with part of the lime replaced by magnesia. Probably due to this replacement, the refractive indices of jurupaite are lower than those of typical specimens of xonotlite, but other properties are substantially identical. The cell dimensions of xonotlite, found by Berman in 1935, are confirmed, but probably refer to a pseudo-cell and not to the true unit-cell. Attention is drawn to the difficulty in reconciling the observed water content of xonotlite with the crystallographic symmetry.

(4) VEATCHITE FROM THE PERMIAN EVAPORITES OF YORKSHIRE.

By Dr. F. H. Stewart, Mr. R. A. Chalmers and Mr. R. B. Phillips.

A few small crystals of veatchite have been found in well cuttings from the D'Arcy Exploration Company's boring at Aislaby in Yorkshire. A microchemical analysis agrees with the formula $SrB_6O_{10} \cdot 2H_2O$. *X*-ray powder photographs are similar to those of material from Lang, California, the only other recorded locality for this mineral. The physical and optical characters of the Yorkshire material are essentially similar to those previously recorded but show minor differences. The mineral is confined to the lower evaporite bed of the Aislaby boring.

The following paper was taken as read:—

(1) THE ORTHOCLASE-MICROCLINE INVERSION.

By Dr. W. S. Mackenzie.

The variable lattice of microcline is discussed and two examples of the association of monoclinic and triclinic potash feldspar are described. The differences in the nature of the change from one form to the other in these two occurrences are considered important for establishing the relation between orthoclase and microcline.

A meeting of the Society was held on Thursday, March 25th, 1954, at 5 p.m., in the apartments of the Geological Society of London, Burlington House, Piccadilly, W.1 (by kind permission).

The following papers were read:

(1) ON BASSETITE AND URANOSPATHITE.

By Prof. C. Frondel.

Re-examination of the original materials described by Hallimond has led to the identification of additional specimens in the Harvard collections, and analyses have been obtained. Bassetite proves to be the ferrous iron compound, not a calcium salt resembling autunite in composition. In uranospathite the non-volatile constituents correspond with a composition between torbernite and zeunerite, though the very low density and refractive index suggest that it will be a higher hydrate. On exposure to normal conditions in the Harvard laboratories both minerals were subject to alteration, with optical changes corresponding with those in the original description, due to loss of water. *X*-ray measurements are given for analyzed crystals from the Harvard material.

(2) MANGANESE AMPHIBOLES FROM SITASAONGI MINE, BHANDARA DISTRICT, INDIA.

By Mr. S. A. BILGRAMI.

Three manganese amphiboles, winchite, juddite, and a new variety, are described together with chemical analyses and optical properties. The winchite occurs in a feldspathic gneiss, the others in pegmatite which cuts a manganese ore band. The chemical composition of these amphiboles is discussed and their possible origin suggested.

(3) TRANSITIONAL OPTICS OF SOME INTERMEDIATE PLAGIOCLASE FELDSPARS.

By Dr. I. D. Muir.

The optical properties of the analyzed andesine from the iron-rich facies of the Beaver Bay diabase are transitional between the standard low- and high-temperature forms. Comparisons made with plagioclases from similar dolerites and gabbros indicate that andesines and labradorites transitional between the true low- and high-temperature states are common. Confirmation of the transitional nature of these plagioclases has been obtained by *x*-ray rotation photographs. After heat treatment the minerals were subjected to a further optical and *x*-ray examination.

(4) Zoned Plagioclases in Layered Gabbros of the Skaergaard Intrusion, East Greenland.

By Dr. J. M. Carr.

A mild zoning affects the primary precipitate crystals of three analyzed plagioclase feldspars from gabbros belonging to the main layered series. Usually it is normal in type and thus shows an outward trend to more sodic material. In one specimen, however, a minority of the crystals possesses oscillatory-normal zoning. The zoning of these crystals progresses through an alternating series of more and less calcic zones towards a final more sodic composition. Both types of zoning are largely ascribed to changes in hydrostatic pressure due to vertical movement of magma and crystals. According to this view, the oscillatory zoning resulted from prolonged circulation of a selection of the feldspars in convecting magma.

The following papers were taken as read:

(1) An Occurrence of a Regular Mixed-Layer Clay-Mineral.

By Mr. H. Heystek (communicated by the General Secretary).

A white clay used industrially occurs near Burghersdorp, Cape Province, South Africa at the contact of dolerite sheets intrusive into shale. Chemical analyses, x-ray data, differential thermal analysis, and base-exchange experiments, of materials taken at intervals between 1 and 15 feet from the contact, indicate that the illite of the shale has been altered to mixed layers in the ratio 1:1 of montmorillonite and hydrous mica.

(2) Two Arfvedsonitic Rhyolite Intrusions from Cloghaneely, Co. Donegal.

By Dr. E. H. T. Whitten.

Petrographic descriptions of two small arfvedsonite-epidote-rhyolite dikes intruding Dalradian quartzite of north-west Donegal are given. Slight compositional variation of the amphibole produces variation in the optical orientation (changing sign and position of optic axial plane) even within the amphiboles of the same slice. The age of the rhyolites is discussed.

(*Titles and abstracts kindly submitted by G. F. Claringbull, General Secretary*)

BOOK REVIEWS

NENDO-KOBUTSU (CLAY MINERALS), by TOSHIO SUDO. No. 178 of the Iwanami Series, 240 pp.+4 fold-in tables, $4\frac{1}{2}'' \times 6\frac{1}{2}''$, cloth bound, 240 yens. Iwanami-shoten, publisher. Tokyo, Japan. 1953.

The book contains six chapters of unequal lengths. Chapter I gives an historical introduction and generalities on clays. Chapter II (77 pp.) describes the laboratory research methods for the study of clays, including their fractionation. It also gives optical properties and x-ray diffraction powder patterns. Comparison of various patterns is shown by means of line drawings. Disorder in layer stacking and differential thermal analysis are discussed. The Philips diffractometer is mentioned briefly. The chapter ends with a description of the electron microscope and its application to clays through metallic shadow casting. Chapter III (68 pp.) is devoted to the properties of clay minerals (crystal structure, thermal properties, and colloid chemistry). It contains over 20 neat structural drawings, some showing individual atoms, others showing the tetrahedra as geometrical solids. Particularly noted is a detailed discussion of isomorphous substitutions in the various chemical formulae. Chapter IV (43 pp.) treats the topic of formation of clay minerals, including experimental artificial synthesis, but with emphasis on geological considerations. Chapter V (5 pp.) touches on practical applications. Chapter VI (8 pp.) presents a classification of platy minerals and shows their structural relationships.

The bibliography on clay minerals numbers 11 pages. Four indexes are given: subject matter, names of minerals and other compounds, names of authors (listed according to the Latin alphabet). Appendix I lists 26 chemical analyses of clays from Japanese localities; 13 out of the 26 analyses total 100 ± 0.50; most of them are recent (less than 10 years old). Appendix II gives 23 indexed powder patterns. Appendix III presents, for each of 36 analyzed specimens: optical constants, chemical analysis, interplanar distances and cell dimensions in Å, and morphological appearance under the electron microscope.

This book is remarkable in that, in spite of its small size, it succeeds in covering all aspects of the study of clay minerals. Its presentation is also worthy of praise. The second reviewer can recommend the excellent figures to the attention of those mineralogists who do not read Japanese.

NOBUHISA UJIIYE AND J. D. H. DONNAY

THE LITERATURE OF GEOLOGY, by BRIAN MASON, 155 pages, lithoprinted. Published by the author. Price, $2.00, postpaid on order accompanied by remittance and addressed to Brian Mason, The American Museum of Natural History, New York 24, New York.

This little book is not as broad in scope as is a similar one by Pearl (Guide to Geologic Literature, McGraw-Hill, 1951) published recently. It has no general description of library facilities, for example, and it does not discuss local publications, theses, or other forms of unpublished geologic information.

It is divided into two parts: General and Regional. The first part is devoted to reference works of various kinds, abstract journals, and lists of selected references in specific fields. In the regional section countries are listed alphabetically under the respective continents. Under each country the following items are given: (*a*) the publication(s) of the official geological survey; (*b*) important geological serial publications; (*c*) the latest geological map; and (*d*) the most useful and up-to-date source of information on the general geology of the country.

In the absence of an index some cross references would have been in order, especially in Part I. For example, Rice's *Dictionary of Geological Terms* is listed under "Glossaries" and not under "Dictionaries"; Hey's *An Index of Mineral Species and Varieties . . .* is listed under "Glossaries" but not under "Mineralogy"; and Tröger's *Spezielle Petrographie der Eruptivgesteine*, which is quite as much a glossary for petrographic names as is Hey's book for mineralogical ones, is listed under "Petrology" but not under "Glossaries." The *Minerva Jahrbuch der Gelehrten Welt*, Walter de Gruyter and Co., Berlin, might well have been included under "Directories"; Albert H. Fay, *A Glossary of the Mining and Mineral Industry*, U. S. Bureau of Mines Bulletin 95, under "Glossaries"; and the *Neues Jahrbuch Referate*, under "Abstracts."

Mason's book is intended primarily for students and instructors of geology, librarians, and practicing geologists. It will be of little use to research workers and specialists in geology because of the number and nature of omissions. Part I, of course, is highly selective and makes no pretense of completeness. Part II, however, should contain all geological serial publications of any consequence. Some 20 bulletins and other geological publications of states are omitted, however, and almost twice that number from the Latin American countries. It is disturbing to find publications like the *Transactions of the Edinburgh Geological Society*, *Geological Bulletins of the British Museum*, *Proceedings of the Liverpool Geological Society*, and some seven others of similar character omitted from the list of geological publications of Great Britain, when only eight are listed. Other European nations do not fare much better.

In spite of these omissions the volume is very useful for many purposes, especially in finding the latest geological map of each state and country and a general treatment of the geology of each country. The logical and consistent arrangement and almost tabular format make for an ease and security in reference not experienced with books where similar information is largely in conventional text format.

EARL INGERSON,
U. S. Geological Survey, Washington, D. C.

STRUCTURE REPORTS FOR 1945–1946. VOL. 10. GENERAL EDITOR, A. J. C. WILSON; SECTION EDITORS: C. S. BARRETT (*Metals*), J. M. BIJVOET (*Inorganic compounds*), J. M. ROBERTSON (*Organic compounds*). Published for the International Union of Crystallography. N. V. A. Oosthoek's Uitgevers Mij, Utrecht. viii+325 pp. (1953). Price 45.- Dutch florins, postpaid. Alternative: Polycrystal Book Service, 84 Livingston St., Brooklyn 1, New York. $12.00.

The gap between the last issue of *Strukturbericht* (Vol. VII, 1939) and current Structure Reports is gradually being filled. With the appearance of the new Vol. 10, there remain only Vols. 8 and 9 to be published. This volume is like the others, with the same division into Metals, Inorganic Compounds and Organic Compounds. Likewise the crystal structure data are so completely reported that usually no reference to the original source is necessary. A valuable feature is the editorial comment, when necessary.

Workers in many fields are finding these reports of great value, and the editors of this international undertaking are to be congratulated for the thoroughness and promptness with which they are carrying out this important task.

L. S. RAMSDELL,
University of Michigan, Ann Arbor, Michigan

EINFÜHRUNG IN DIE KRISTALLOGRAPHIE by HANS SCHNEIDERHÖHN, Professor of Mineralogy and Petrology, University Freiburg i Br., large octavo, pp. 360+xvi, atlas of 102 plates containing 456 figures, 2 folding plates, cloth. Verlag Karl Alber Freiburg i Br. (1949), price DM 40.

Professor Schneiderhöhn has written a textbook of crystallography that covers the entire field in a nonmathematical approach. It was conceived with the idea that this subject is of interest not only to mineralogists and physicists, but also to chemists, economic geologists, mining engineers, foresters, and biologists.

The book is divided into seven parts: crystal geometry, crystal chemistry; introductory crystal physics; mechanical, thermal, electrical, and magnetic phenomena of crystals; crystal optics; optical crystallographical methods of investigation with the polarizing microscope; and "Erzwungene Anistropie" that embraces electro-optical and magneto-optical effects, optical phenomena induced by strain, optical anomalies, birefringence in colloidal systems, "form" and "streaming" birefringence, and liquid crystals.

The book is divided into texts and plates, each of which is bound separately. The text is so bound that the plates fit into a recess in the binding. Two tables are also fitted into a flap in the back cover. Table 1 gives the periodic system. Table 2 covers the symmetry properties of the 32 crystal classes and is a very useful summary. The plates are in black and white. However, in the section on the polarization microscope, the various colors are indicated by the use of heraldic symbols employing dots and hatchings. There has been collected in this book a considerable amount of information that heretofore has been available only in scattered sources. Teachers will find this information useful as supplementary lecture material.

Professor Schneiderhöhn treats the subject from the phenomonological approach. There is a very careful integration of the text and the atlas of plates. The figures in these plates are well selected and excellently drawn. The coverage is rather complete and includes such subjects as luminescence, the character of optically active crystals, and brief descriptions of the polarization microscope and accessories.

This book will prove both stimulating and useful to those who add it to their library.

George T. Faust,
U. S. Geological Survey, Washington, D. C.

THE COMPOSITION AND ASSAYING OF MINERALS by John Stewart-Remington and Wilfred Francis. Pp. 127+viii, cloth. Published by The Philosophical Library, Inc., 15 East 40th St., New York 16, N. Y. (1953), price $5.50.

The authors have prepared this book as an introduction to the investigation of the chemical composition of minerals. The audiences to which it appears to be directed are those who are concerned with the mining, milling, and utilization of minerals, ores, and rocks.

The book is divided into five parts. Part I deals with methods of qualitative analysis. Dry and wet tests are briefly summarized. This section is designed to help plan the chemical analysis by wet methods. Part II (89 pages) describes the principal metallic minerals and gives qualitative tests and quantitative assays for the major metals. The minerals, with some exceptions, are classified according to the principal metal. This section closes with the quantitative estimation of acidic radicals, viz: chlorine, phosphorus, silica, and sulfur. Part III gives typical assays of ores. Part IV (11 pages) treats the nonmetallic minerals. Three and one-half pages are devoted to a "General Scheme for the Analysis of Silicate Minerals"! The book closes with Part V, which consists of various chemical and mathematical data and a chart giving a "General Qualitative Analysis Scheme for Metals."

The mineralogical nomenclature is decidedly antiquated. Thus "crocosite" is used for crocoite, "alumstone" for alumite, etc. Furthermore, terms not previously in use such as "millorite" for millerite and "calcium uranate" for autunite are introduced.

The book contains a number of typographical errors that tend to confuse the nomenclature. The text itself is not free from errors, i.e., on p. 18, mercury when "frozen is cubic the crystals being octahedral"; on p. 27, tenorite is "very common in the Copper Mines of the Mississippi Valley, U. S. A."

The reviewer would not recommend this book for students; its subject matter is treated with too great a brevity to make it a usable text. Industrial analysts may find some helpful suggestions.

George T. Faust,
U. S. Geological Survey, Washington, D. C.

IDENTIFICATION AND QUALITATIVE CHEMICAL ANALYSIS OF MINERALS

by Orsino C. Smith. Second Edition, pp. 385+ix. Published by D. Van Nostrand Company, Inc. (1953), price $7.50.

A review of the forerunner of this book was published in this *Journal* in volume 25, page 767, 1940, and of the First Edition in volume 32, page 253, 1947. The present edition has 34 more pages than the first, which represents a ten percent increase. This expansion is spread over several chapters and includes a new section on the "History of blowpiping." There has been some rearrangement of the contents. The author has endeavored to improve the text on the basis of suggestions from those who use the book in the class and in the field.

The identification tables have not been changed. In the preface to the Second Edition, the author writes:

> "Because of the new methods now in use in studying the structure and composition of minerals, it is being found that a number of substances which have been classified as distinct minerals are variations of other minerals, mixtures, etc., with the result that name changes and cancellations are in progress. This checking may take some time, and it is thought inadvisable to attempt to reclassify the minerals until this process is more complete."

Presumably, this refers to the completion of volume 3 of Dana's System of Mineralogy, seventh edition.

George T. Faust,
U. S. Geological Survey, Washington, D. C.

TAFELN ZUM BESTIMMEN DER MINERALE NACH ÄUSSEREN KENNZEICHEN

by H. v. Philipsborn, $7\frac{1}{4}'' \times 10''$, xxvii+244 pp., 10 plates with 289 crystal drawings, and 1 illustration in the text. E. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, Germany, 1953. Price, Cloth-bound, DM 17.

The first set of tables for the rapid determination of minerals based upon the recognition of their physical properties, such as luster, color, streak, and hardness, was published in 1866 by Professor Albin Weisbach of the Saxon School of Mines, Freiberg, Germany. The Weisbach tables were used extensively and passed through thirteen editions. Friederick Kolbeck was responsible for the sixth to the thirteenth (1923) editions. The main portion of this text, pages 1–167, by H. v. Philipsborn, who succeeded Weisbach and Kolbeck at the Saxon School of Mines, is an extension of their tables, and the volume is very fittingly dedicated to them.

The number of minerals included in the tables is large, for there are 568 entries with few duplications. The tables are subdivided according to luster, color, and streak, and the minerals arranged in order of increasing hardness. Other physical properties, chemical composition, mineral associates, occurrences, and similar minerals are given.

In addition to the main tables, the author has compiled very helpful determinative tables based upon (1) Morphological Features, pages 168–184, supplemented by 289 crystal drawings; (2) Chemical Properties, pages 185–218; and (3) Microscopic-optical Properties, pages 219–236. There are many cross-references in all tables.

The various terms, properties, methods, and reagents referred to in the tables are fully explained in the introduction, pages xi–xxvii, which also includes a table of abbreviations, an extensive bibliography, and a very helpful listing of equivalent terms and expressions in five languages. There is a very good index.

The author has made a major contribution to determinative mineralogy by incorporating in a single volume so many helpful tables. The book, which is obviously the result of much time and effort, is well printed and reasonably priced.

Edward H. Kraus,
University of Michigan, Ann Arbor, Michigan

NEW MINERAL NAMES

Chinoite

C. W. Beck and D. B. Givens, Chinoite, a new mineral. *Am. Mineral.*, **38**, 191–196 (1953).

Discussion: It is pointed out by C. Guillemin, *Bull. soc. franc. mineral., crist.*, **76**, 367–369 (1953), that chinoite has certain properties that are nearly identical with those of libethenite and suggests that further study is needed. Following is a comparison of the data on the two minerals.

	Chinoite	*Libethenite*
Composition	$Cu_5(PO_4)_2(OH)_4$ (*a*)	$Cu_4(PO_4)_2(OH)_2$ (*a*)
Color	Dark emerald-green	Olive-green
Crystal System	Orthorhombic, *Pnn*	Orthorhombic, *Pnn*
Axial ratio, goniometric	0.8967:1.0:0.7046 (*b*)	0.9606:1:0.7024
Structure a_0	7.47 Å	8.08 kx
cell b_0	8.31 Å	8.43 kx
c_0	5.83 Å	5.90 kx
Cleavage	{110} perfect	{100} and {010} very indistinct
Fracture	Irregular	Conchoidal to uneven
Hardness	5–6	4
Sp. gr.	5.22 (*c*)	3.97
Optically	Positive	Negative
2 V	Near 90°	Near 90°
Indices, α	1.698	1.701–1.704
β	1.745	1.743–1.747
γ	1.793	1.787–1.790
Orientation	$X=c$	$X=b$
X-ray powder data	Essentially identical (*d*)	

(*a*) Chinoite, analysis by M. E. Carlisle on 240 mg. P_2O_5 24.33. CuO 69.09, H_2O 6.57% Libethenite, analysis by Bergemann (1890) from Libethen, P_2O_5 26.46, CuO 66.29, As_2O 2.30, H_2O 4.04%.

(*b*) From measurements on 3 forms. For {110}, phi = 48°07′ (corresponding form o libethenite 46°09′); for {011}, rho = 35°10′ (corresponding form on libethenite 35°05′).

(*c*) Guillemin points out that the data of Beck and Givens ("The crystal used in th specific gravity determination weighed 6.26 mg. in air, 3.17 mg. in CCl_4, from which a specific gravity of 5.22 was indicated, a close check with the theoretical value, 5.24") actually yield a specific gravity of 3.24.

(*d*) The *x*-ray powder data cited by Guillemin (source not stated) agree with those o the *A.S.T.M.* file.

Michael Fleischer

Osumilite

Akiho Miyashiro, Osumilite, a new mineral, and cordierite in volcanic rocks. *Proc. Japa Acad.*, **29**, 321–323 (1953).

This is a preliminary account; details are to be published in the *American Mineralogis* The mineral occurs in biotite-bearing hypersthene-plagioliparite (rhyodacite) in Sakkabira Tarumizu-mati, Kagosima Prefecture, southern Kyûsyû, Japan. It was originally though to be cordierite, but is a distinct mineral. The composition is (K,Na,Ca) (Mg,Fe'')

$(Al,Fe'',Fe''')_3(Si,Al)_{12}O_{30}\cdot H_2O$. It is hexagonal (dihexagonal-dipyramidal) with a_0 10.17, c_0 14.34 Å. The space group is $C6/mcc$ (D^2_{6h}). Structurally the mineral is composed of hexagonal double rings $(Si,Al)_{12}O_{30}$. It is optically positive, nearly or completely uniaxial, with α or ω 1.545–1.547, γ or ϵ 1.549–1.551; birefringence 0.004; 2 V over Z usually 0–70°; pleochroic in thin section with *O* light blue, *E* colorless. Several "cordierites" described in the literature from volcanic rocks may be osumilite. The name is for the Ôsumi Province.

M. F.

NEW DATA, REDEFINITION OF MINERALS

Cannizzarite

A. R. Graham, R. M. Thompson, and L. G. Berry. *Am. Mineral.*, **38,** 536–544 (1953).

Benjaminite

E. W. Nuffield. *Am. Mineral.*, **38,** 550–552 (1953).

Renierite

Joseph Murdoch. *Am. Mineral.*, **38,** 794–801 (1953).

Stevensite

G. T. Faust and K. J. Murata. *Am. Mineral.*, **38,** 973–987 (1953).

Thorogummite

Clifford Frondel. *Am. Mineral*, **38,** 1007–1018 (1953).

Mosesite

George Switzer, K. J. Murata, J. J. Fahey, and W. F. Foshag. *Am. Mineral.*, **38,** 1225–1234 (1953).

Billietite

J. W. Frondel and Frank Cuttitta. *Am. Mineral.*, **38,** 1019–1024 (1953).

Becquerelite

J. W. Frondel and Frank Cuttitta. *Am. Mineral.*, **38,** 1019–1024 (1953).

Niggliite

Paul Ramdohr. Neue Erzmineralien (abstract). *Fortschr. Mineral.*, **28,** 69–70 (1949) (Published 1950).

It is stated that niggliite, supposedly $PtTe_3$, actually has the composition PtSn.

M. F.

Allargentum

Paul Ramdohr, Neue Erzmineralien (abstract). *Fortschr. Mineral.*, **28,** 69–70 (1949) (Published 1950).

Name given to the hexagonal phase known in the synthetic system Ag-Sb, Ag containing 8 to 15% Sb. Found associated with dyscrasite and cubic antimonian silver from Cobalt, Ontario.

M. F.

Eskebornite

Paul Ramdohr, Neue Erzmineralien (abstract). *Fortschr. Mineral.*, **28,** 69–70 (1949) (Published 1950).

Name given to a mineral, perhaps FeSe or (Fe,Cu)Se, from Tilkerode, Harz Mountains. Very similar to pyrrhotite in physical properties, but much softer. Magnetism highly variable according to orientation. Optically hexagonal or pseudo-hexagonal, but the x-ray pattern is cubic, similar to that of sulvanite.

M. F.

Y. Takeuchi, The crystal structure of magnesium pyroborate. *Acta Cryst.*, **5**, 574–581 (1952).

Material from the Suan mine, North Korea, gave B_2O_3 40.08, MgO 46.63, CaO 5.06, SiO_2 0.60, $(Al,Fe)_2O_3$ 0.63, H_2O^+ 0.90, H_2O^- 0.23, CO_2 5.06; sum 99.19% (given as 99.46%); analysts N. Saito and N. Kokubu. This corresponds, after deducting $CaCO_3$ and other impurities, to $Mg_2B_2O_5$. Weissenberg and rotation photographs show it to be monoclinic, the unit cell has $a=12.10\pm.05$, $b=3.12\pm.02$, $c=9.36\pm.05$ Å, beta 104°20′±30′, containing $Mg_8B_8O_{20}$. The space group is $C^5_{2h}-P2_1/a$. X-ray powder data are given. The occurrence will be described in a later publication.

M. F.